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Metals and Alloys

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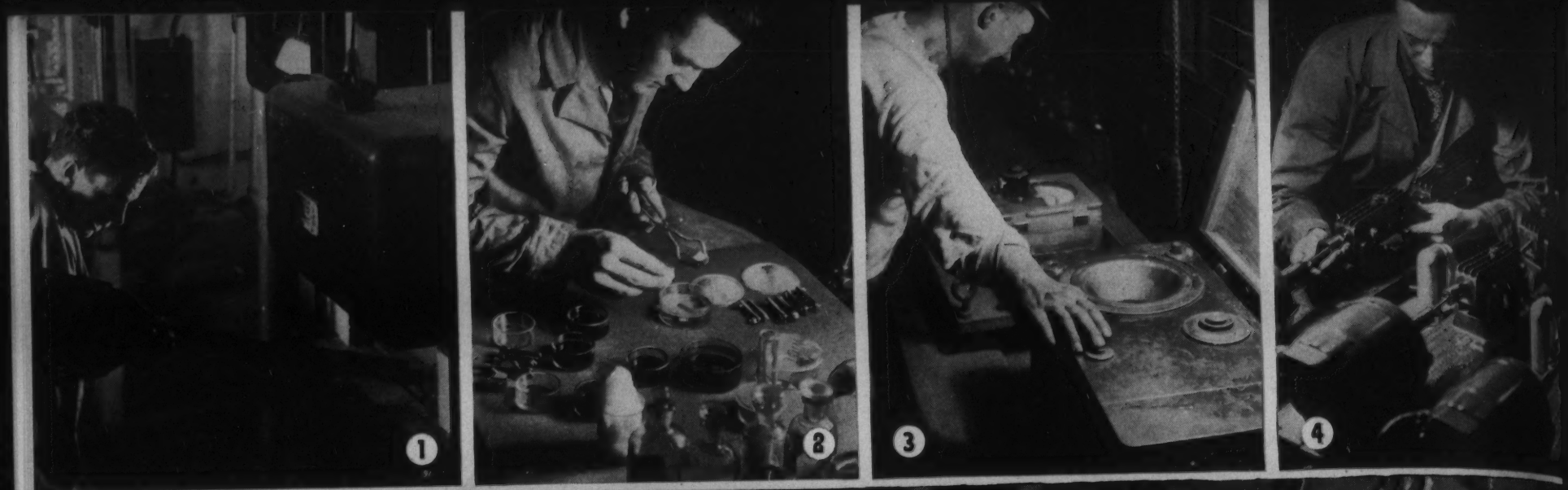


THIS IS WHAT WE MEAN WHEN WE TALK ABOUT...

9

A FEW OF THE TESTS WE MAKE TO BE SURE YOUR STEEL IS RIGHT

1. Heating small billet for experimental rolling on laboratory mill.
2. Etching a specimen of steel for subsequent examination under the microscope.
3. Carbometer test in open-hearth for carbon analysis.
4. Testing the behavior of steel under repeated alternating stress in fatigue machine.
5. Heating sample bar for experimental quenching and tempering.
6. Microscopic examination for grain size.
7. Ascertaining hardenability by examination of fractured samples and etched sections.
8. Rockwell test for hardness.
9. Metallurgical observer checking teeming temperature on pouring platform.

USS

How Much Ductility!

We cheerfully use cast iron, with no measurable elongation. Many of the older cast aluminum alloys have served, and still serve nicely, without ductility. In the days of the Liberty motor, a definite ductility figure and a definite impact figure were required on crankshafts. It would have been heresy to suggest a crankshaft material other than forged, heat-treated alloy steel with high toughness for its strength.

Yet the Ford crankshaft material, showing very low ductility at best and, in heavy sections cut from actual crankshafts, practically none at all, serves excellently in millions of cars.

Great pains have been taken to use carburizing steel of high core impact and ductility for automobile gears, but the toughness of the gear itself, with its relatively brittle case, is low and not very much affected by the toughness of the core when the case is removed. Hence the requirement of core toughness no longer looms very large.

Some engineers say that even when one desires full insurance against brittle failure, there is no point in demanding more than 10 per cent elongation. Initial ductility is not always maintained, some of the very early 18 and 8 tubes used in oil refining, failed in brittle fashion without bulging, despite the high ductility as installed.

Actually, ductility, as such, is utilized in fabrication rather than in service. Ability to be cold drawn, forged or rolled, or to be bent, pressed and deep drawn, depends on many things other than elongation and reduction of area.

Percentage elongation is really used only as a sort of sign post, to give hints as to energy absorption, the area under the stress strain diagram, or to assure similarity to materials that have done well in service, irrespective of whether the service involves deformation. If we shift from one class of materials to another, for example, from one of high elongation and low damping to one of low elongation and high damping, we take the change in ductility as a matter of course, since there has been a degree of compensation.

Actually, we are more often concerned with propensity toward notch propagation than with ductility. Since we can much more readily evaluate the latter than the former, we tend to draw specifications in terms of high ductility, in a rather child-like hope that we'll get resistance to notch propagation.

The steel foundrymen struggle to get the 22 or 25 per cent elongation demanded by the specification. The more ductile casting is doubtless no worse than one of only 18 or 20 per cent, but in what service will this difference govern success or failure? What's sacred about 22 per cent?

Regular malleable iron castings have been shoved up from under 10 per cent elongation to around 20 per cent, largely at the insistence of the producers rather than the consumers of malleable. In the process of shoving up the ductility, a tacit condemnation of material with 5 to 10 per cent elongation has been built up, which militates against the acceptance of the very much stronger short-cycle, pearlitic, malleable which, on the basis of a summation of all its properties, seems to be a better engineering material than regular malleable.

One may justly ask whether high ductility in the tensile test is not merely a fetish, insistence upon which may not at all serve the underlying purpose of evaluating some more elusive property that we really want but cannot so readily measure, and (sometimes) cannot even define.

The National Advisory Committee for Aeronautics, if we recall correctly, has asked the National Bureau of Standards to look into this problem of how much ductility is needed in a metal. We don't envy them the task of giving the answer, but we are pleased that the question has been put. Even if no answer can be given, a serious discussion of the problem, published by the Bureau, will go far toward disabusing the designer of the idea that he necessarily has a sacred duty to demand a high percentage of elongation whether or not it connotes the condition the service really demands.

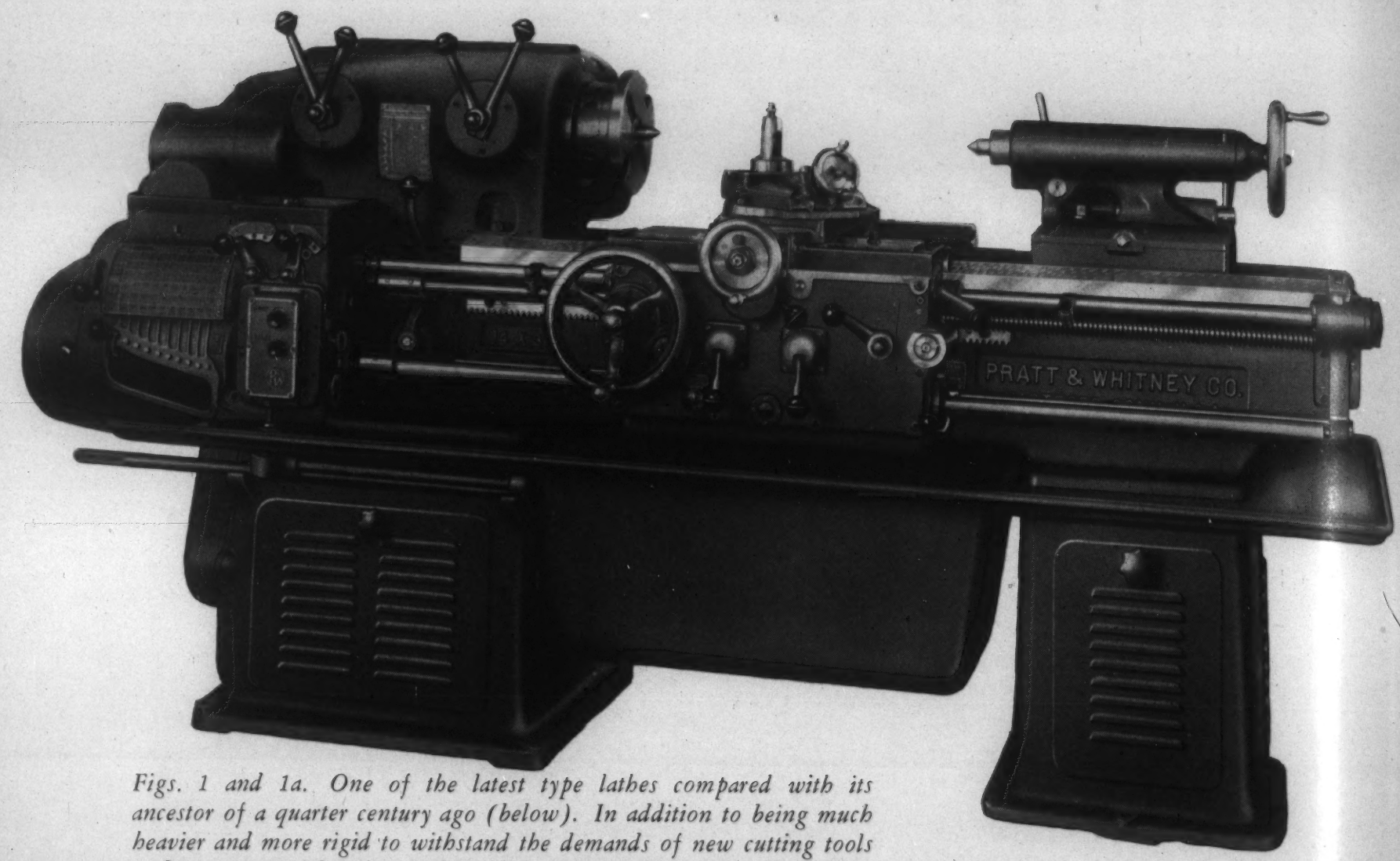
If the blind belief in ductility can be wiped away, we will then be in position to open our eyes to the next question, which is—"what tests will truly evaluate the properties really needed for performance?" The answers to this may be various. Repeated bend tests; impact tests with a range of specimen sizes, and over a range of temperatures; notched fatigue tests,

(Continued on page 289)

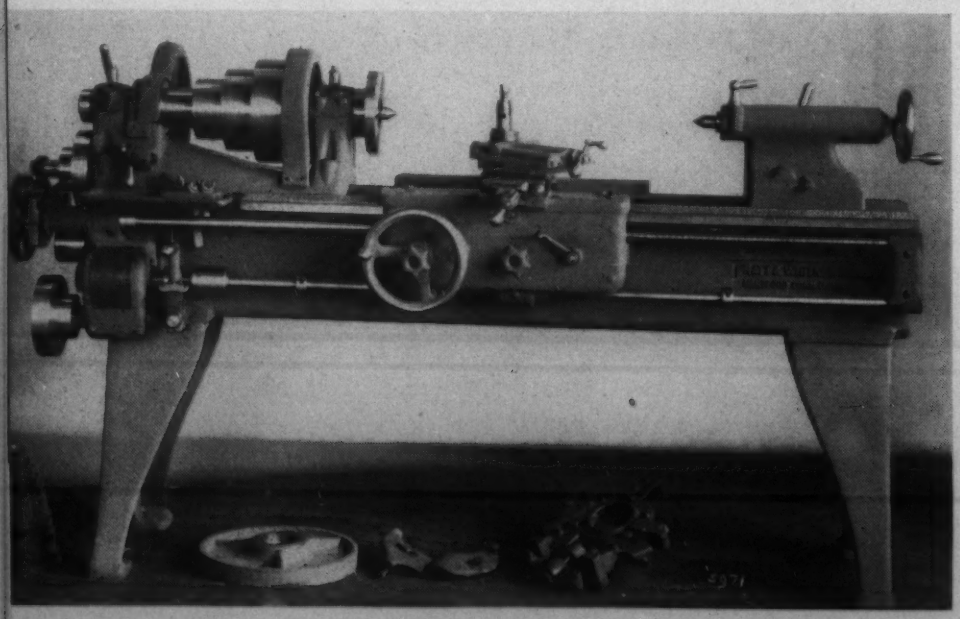
Role of Nickel in the

BY J. W. SANDS AND D. A. NEMSER

The International Nickel Co., Inc., New York



Figs. 1 and 1a. One of the latest type lathes compared with its ancestor of a quarter century ago (below). In addition to being much heavier and more rigid to withstand the demands of new cutting tools and new materials, the modern lathe incorporates such features as hardened and ground alloy steel gears and multi V-belt drive. (Courtesy: Pratt & Whitney, Division Niles-Bement-Pond Co.)



In the last few years, and particularly in the last 10 years, the materials which have been incorporated in the general run of machine tools have been undergoing almost a radical revolution as to composition. There has been a wider use of alloy cast irons and steels and of non-ferrous alloys which has resulted in machines insuring greater accuracy and efficiency. A broad survey of this evolutionary trend is furnished in this article by authorities very close to the industry. It is a revelation of the application of metallurgical engineering to an industry which is basic in its nature.—The Editors.

Machine Tool Industry

A MACHINE TOOL may be defined as an adjustable machine operated by other than hand power employing a cutting tool for the forming of parts by the removal of excess stock. Usually machine tools operate on metals, but may also be used in connection with wood, plastics and other non-metallic materials. This classification excludes those types of metal working machinery which do not operate by removal of metal, such as sheet metal working, welding, wire drawing and wire working machines, but does include grinding machines.

Basic Machines of Industry

It is obvious that machine tools are the basic machines of industry and are unique in that they are the only machines which perpetuate themselves. Hence the machine tool industry may be regarded as the parent industry of all modern manufacturing. The industry began to take shape in something like its present form soon after the Civil War, although Eli Whitney, best known as the inventor of the cotton gin, is credited with its actual inception in 1798 when he contracted to manufacture several thousand rifles for the United States Government. To carry out this undertaking he designed and built the necessary machine tools together with the required jigs, fixtures and gages, thus establishing the American system of interchangeable manufacturing—the forerunner of mass production.

The industry gained initial prominence in New England, but, while this territory is still an important factor, Ohio now ranks first in production with the Cincinnati region outstanding. The Rockford area in Illinois is also a large producer. The entire industry is concentrated in a relatively small number of plants, somewhat over 250 being in operation at the present time.

Improvements in the Last Ten Years

Within the last two or three decades, and particularly in the last 10 years, the machine tool industry has made remarkable improvements in the quality of its products in a successful effort to keep abreast of the increasingly heavy demands made upon these machines by modern manufacturing methods. Although the earlier machine tools were fully adequate for the requirements of their day, judged by present standards they would be considered of rather poor grade, both as to durability of the machines themselves and the quality of the work which they turned out. This was due to a number of factors, including the use of unalloyed cast iron gears and bushings, plain carbon steels for stressed or wearing components, slow speeds, lack of accuracy, poor tolerances, lack of rigidity due both to design and materials, and poor tool life resulting from lack of metallurgical knowledge of high-speed steel. Parts wore out or broke so rapidly that their replacement constituted a sizable portion of the business of the industry.

The present picture is quite different. With the application of alloy steels and cast irons, bronze bushings, pre-loaded anti-friction bearings and other modern innovations, today's machine tools can not only turn out extremely accurate work at vastly higher speeds but are inherently so reliable and durable that failure of parts has been almost completely eliminated. In fact, parts replacement, far from providing an added source of income, has become an item of expense to the manufacturer since the failure of a machine tool component in the field now usually involves a visit by a service man from the manufacturer's plant to make the repair. The ruggedness of modern equipment is reflected in the fact that, although the newer machines incorporate marked improvements, less than 5 per cent of the equipment now in service has been purchased since 1936.

Modern Machines and Their Predecessors Compared

Modern machine tools when compared with predecessors of as recent a vintage as 10 years ago are more powerful, more sturdy, more accurate, more easily controlled and more pleasing in appearance. Incorporating such advances as the pre-loaded bearings already mentioned, V-belt drives, hydraulic control, automatic lubrication, bronze bushings, pneumatic devices, improved cutting tools, carefully selected alloyed materials for all vital parts, and modernistic design, they are capable of handling harder and tougher materials at high speeds without distress and with extreme accuracy. (Fig. 2). They are so rigid that they can operate with cemented carbide tools without vibration or chatter at spindle speeds up to 3000 r.p.m. or more.

While this metamorphosis has been due in a large part to improved design, it would have been completely impossible without the availability of construction materials capable of handling the higher unit stresses involved and sufficiently wear resistant to maintain the high accuracy and smoothness of operation desired. These materials, in turn, owe their superior properties largely to their alloy content. One of the most important of these alloys is nickel, as is clearly indicated by the fact that

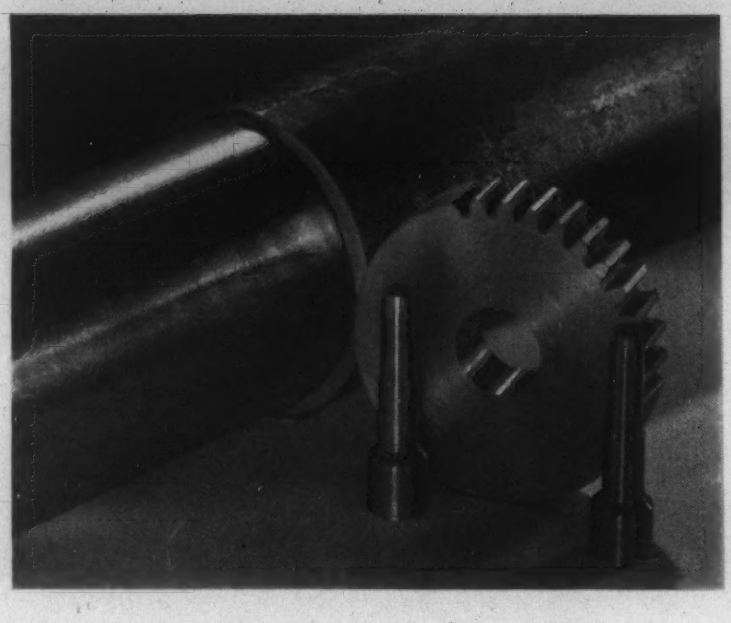


Fig. 2. Gear blank and test bars machined from nickel-chromium-molybdenum steel at 477 Brinell hardness. (Courtesy: Jos. T. Ryerson & Sons.)

more than four out of every five of the leading machine tool producers employ nickel containing steels and cast irons for major components. In this article it is proposed to discuss the role of nickel in the machine tool industry from the standpoint of both consumer and producer.

CAST IRON.—The Basic Material

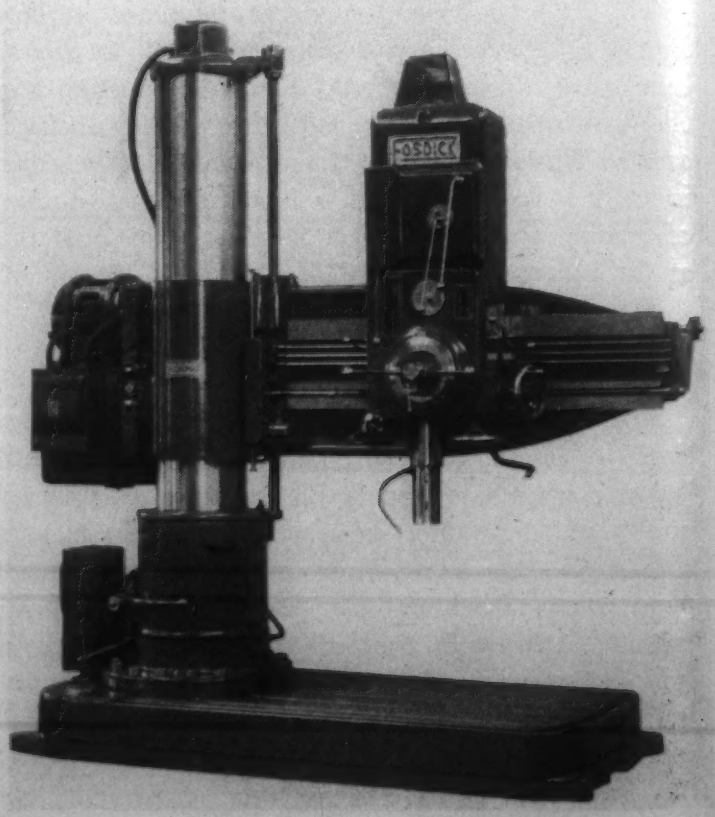
Cast iron is and always has been the basic material of the machine tool industry. While conventional machines no longer employ it to any great extent for such parts as gears and spindles, cast iron remains the preferred metal for the more massive components such as bases, beds, tables, saddles, columns and the like. Even for some of these parts, however, its supremacy is occasionally challenged by the proponents of welded steel construction. An evaluation of the merits of the pros and cons of this argument is beyond the scope of this discussion, but the case for the welded steel has been ably presented in a recent paper by Nenninger and Maddox.[1]

Very often the scope and range of quality embraced in the term "cast iron" are not appreciated. The metal has a number of definite and distinct advantages which render it an extremely useful engineering material. Cast iron is easy to handle, is low in cost, and possesses good machinability, good resistance to wear, excellent damping properties and high compressive strength. In comparison with steel it has lower tensile strength and modulus of elasticity, and is not ductile. These properties, however, may be greatly improved by alloying and processing, so that today cast irons are readily available which are entirely suitable for applications requiring relatively high strength and stiffness. Components carrying overhanging arms or columns, such as the ram on a shaper or the arm of a radial drill, fall in this class since bending moments are high and rigidity is of great importance. (Fig. 3).

The metallurgy of cast iron is an exceedingly complex subject which is far more involved than that of steel. Despite this fact, it is unfortunately true that in the past the material has been more or less neglected from a research point of view and it is only recently that it has become the subject of any thorough research effort. Heretofore, for example, it has been customary to regard hardness as a direct measure of wear resistance, whereas intelligently directed microscopic study indicates that hardness does not tell the whole story inasmuch as the presence of free ferrite, massive carbides or dendrites in the structure of cast iron interferes with wear resistance.

This discovery was of immediate practical importance in checking a growing tendency on the part of many machine tool foundries to obtain a high strength dense iron for larger machine tool castings by the use of high percentages of steel in the charge. The steel, in some instances, ran as high as 90 per cent, resulting in a low total carbon content, usually under 3 per cent, and consequent lack of an adequate quota of graphite. These irons manifest "short life" and consequently set up rapidly in the mold. This under-cooling effect together with the low graphite content causes a retention of the dendritic pattern, poor distribution of graphite and, in certain cases, the presence of free ferrite. All

Fig. 3. Radial drill with inner column of nickel cast iron to provide high strength and stiffness. (Courtesy: Fosdick Machine Tool Co.)



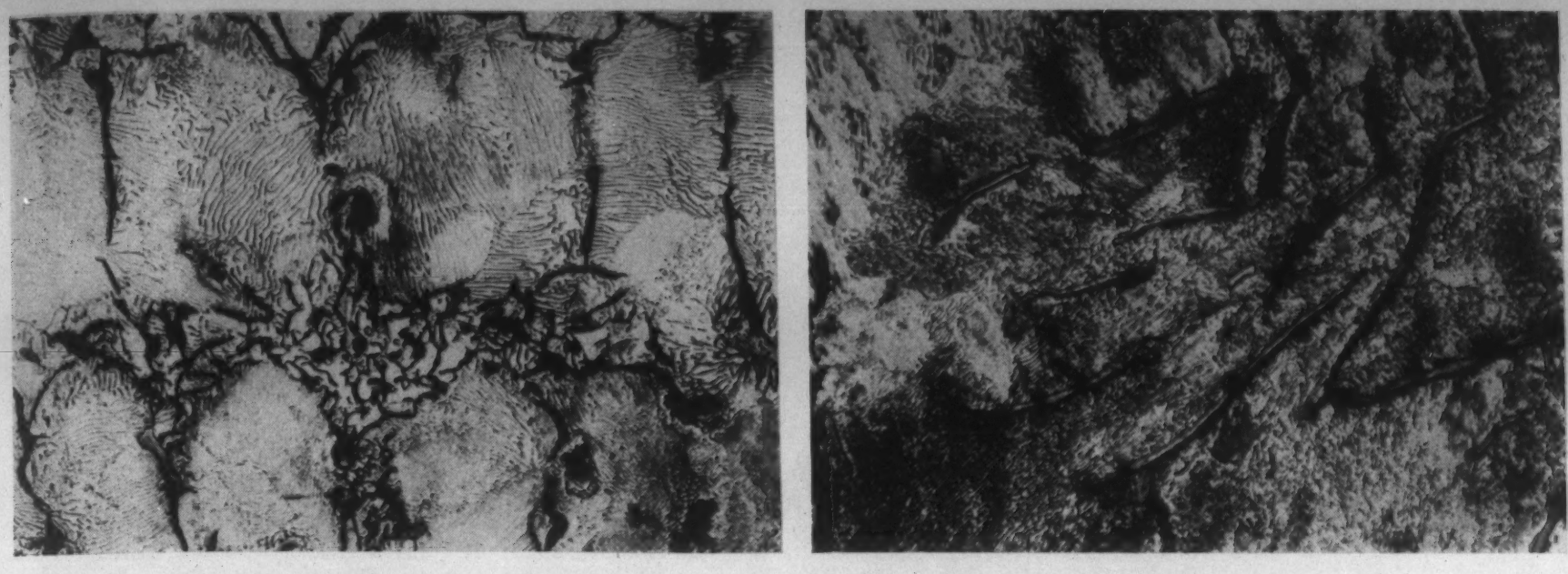


Fig. 4. Poor wearing structure (left) showing dendritic pattern, free ferrite and poor graphite distribution, and (on right) preferred structure with normal graphite distribution, no free ferrite and uniformly fine pearlite matrix. (Nital etch. X 500).

of these effects contribute to the galling of reciprocating parts. Reduction in the amount of steel and lower silicon content plus a ladle addition of ferrosilicon and nickel will prevent the formation of fine graphite and primary ferrite and produce a dense iron of higher total carbon content which, nevertheless, is more resistant to galling and wear. Examples of a satisfactory and an unsatisfactory structure are shown in Fig. 4.

In those more or less massive machine tool castings for which a high strength level is not required and for which the tendency is to employ sections sufficiently heavy to insure suitable rigidity, the fundamental requisite is a uniform close grained structure on exposed surfaces combined with good machinability. Although this may sound simple, the condition is not so easy to achieve in large castings or those with variable section or those in which deep slots must be machined. Control by the ordinary method of varying silicon and total carbon contents is often unsatisfactory owing to the difficulty of obtaining a uniform, dense, machinable gray structure throughout the castings.

Compositions adjusted to develop close grain in the heavy sections frequently result in unmachinable white or mottled structures in ribs, webs, oil pans and similar light areas, whereas increasing the silicon content to insure grayness in these regions will induce coarseness and porosity in the heavy sections. Furthermore, even in large castings of relatively uniform section a composition adjusted to the section may produce chilled edges or corners. Thus a lathe bed employing a low silicon iron to develop a close grain on the machined ways may introduce severe machining difficulties on the edges or corners.

The increasing popularity of hydraulic controls to replace gear trains for the purpose of achieving precise and smooth control of moving parts has emphasized the problem. Hydraulic castings are

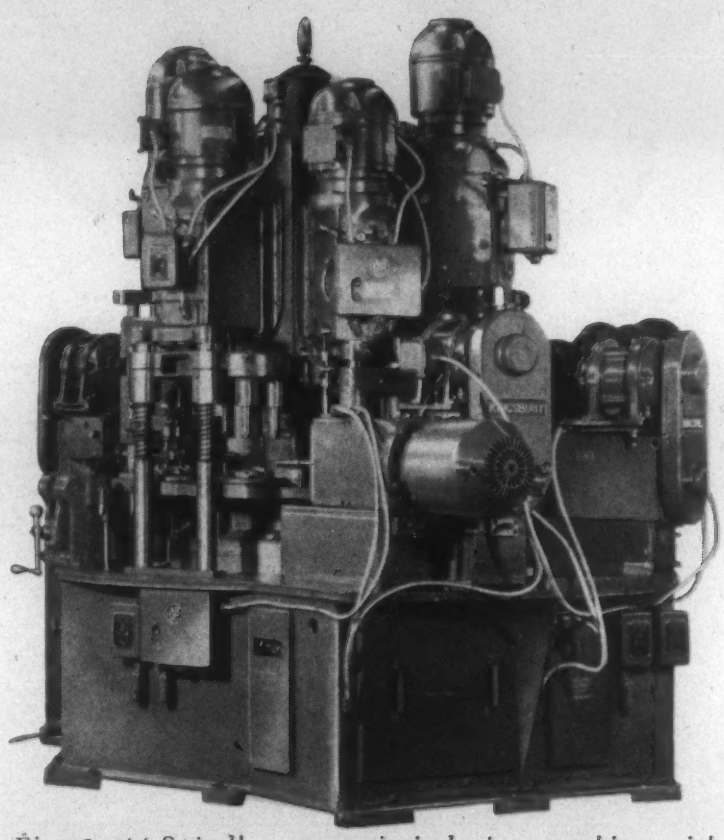


Fig. 5. 44-Spindle automatic indexing machine with index table of nickel cast iron. (Courtesy: Kingsbury Machine Tool Corp.)

usually quite heavy and are perforated to allow for passage of the liquid. No porosity can be tolerated since this will cause leaks and so reduce the efficiency of the control mechanism. When these castings were first produced attempts were made to obtain the desired density by the use of chills, but this procedure was found to be unreliable and it is now the general practice to resort to alloyed irons.

Effects of Nickel on Cast Iron

It is to overcome difficulties of the kind discussed above, rather than to obtain improved strength and stiffness, that nickel is used in castings of the type under consideration. Nickel, like silicon, is a chill reducer, but it differs from silicon in that it controls chill without appreciably coarsening the graphite structure or grain and without lowering the strength. It is obvious that this is the type of action required to counteract the coarsening effect of ordinary meth-

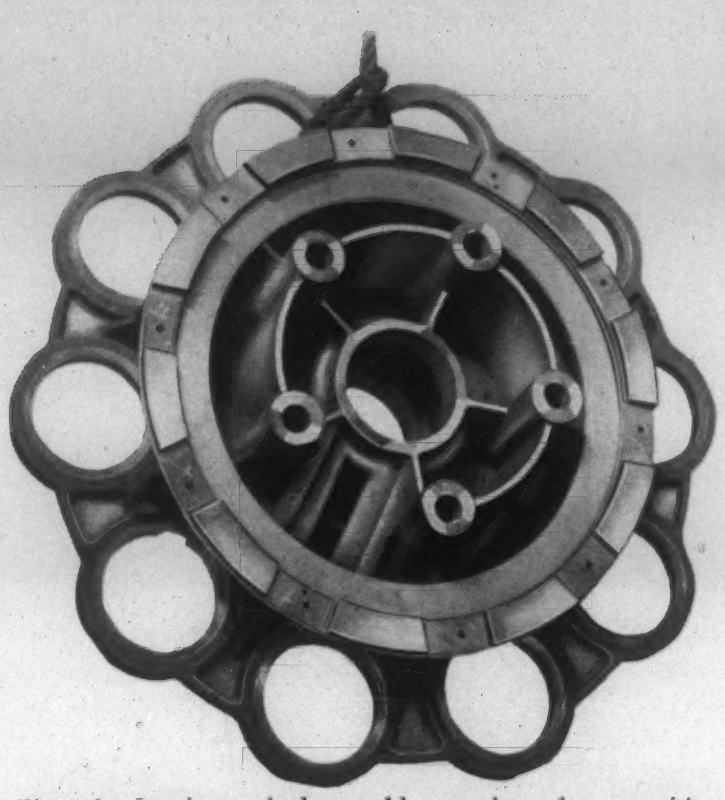


Fig. 6. Intricate index table casting for machine shown in Fig. 5. Uniform structure and good machinability maintained by use of nickel despite sharp changes in section.

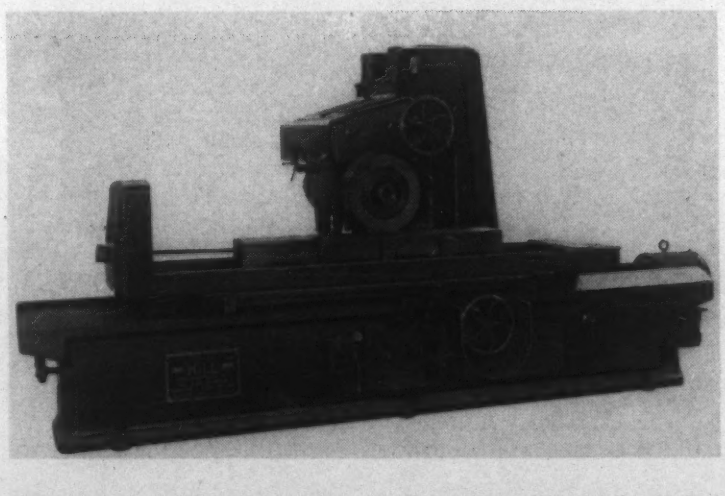


Fig. 7. A 60-in. hydraulic surface grinder with nickel cast iron bed, table, columns and chuck surfaces. (Courtesy: Hill Clutch Machine & Foundry Co.)

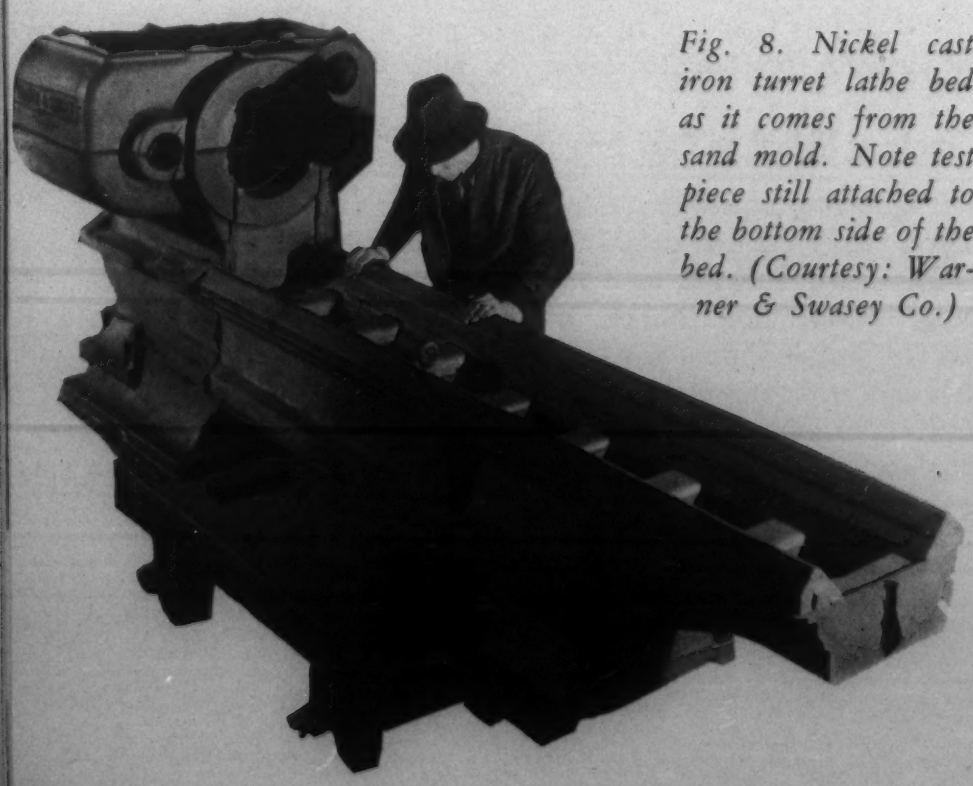


Fig. 8. Nickel cast iron turret lathe bed as it comes from the sand mold. Note test piece still attached to the bottom side of the bed. (Courtesy: Warner & Swasey Co.)

ods of reducing chill and to avoid the local or general formation of free iron carbide.

In chill reducing power nickel is approximately half as effective as the same quantity of silicon. It can, therefore, be used effectively to replace a part of the silicon. The advantages of lowering the silicon content are well recognized. Low silicon iron is denser and of finer structure, contains more combined carbon and is harder and stronger. The simultaneous presence of nickel stabilizes the high combined carbon content throughout the casting and maintains it at a level which insures a steel-like (pearlitic) matrix consisting of an intimate mixture of iron and iron carbide, rather than the less desirable nearly pure iron (ferritic) structure which obtains when the matrix is deficient in combined carbon. Stabilization of combined carbon in heavy and light sections results in a uniform structure and consequent freedom from internal casting stresses, the subsequent release of which might cause distortion of the part.

The addition of nickel, therefore, allows one to obtain all the benefits of a low silicon iron without any of the disadvantages, which include excessive chilling, decreased machinability, non-uniform matrix structure and internal casting stresses. When the general statement is made that nickel refines the grain of iron and increases its strength, reference is made to iron in which nickel has replaced a portion of the silicon in proper and equivalent measure.

The general principle followed in the manufacture of these machine tool castings is to lower the normal silicon content and to add the requisite amount of nickel to insure a fine grained graphite, reduce chill, obtain a uniform concentration of combined carbon in all sections and maintain machinability. This is the general principle, but its application to individual machine tool parts can not be summarized simply and concisely, as the composition of each casting must be adjusted in the light of its size and shape and the particular characteristics desired.

Frequently nickel is not originally specified but is used as a beneficial measure when it becomes apparent that plain iron is not adequate for the application. The method of employing it then depends on the factors in which the original iron is deficient. If, for example, hydraulic castings are being produced which are entirely sound, strong, and of suitable composition, but are difficultly machinable, it is only necessary to add sufficient nickel to reduce chill and restore machinability without other adjustments of the original composition. If, on the other hand, castings are unsound on test and foundry rejections are high due to shrinkage and porosity, the silicon content should be reduced and enough

nickel added to compensate, in point of chill, for the silicon reduction.

Additions of Cr and Mo

In certain cases, particularly when relatively heavy sections are involved, it is sometimes desirable to supplement the nickel with an addition of chromium. With respect to its effect on iron, chromium resembles nickel in some features. It refines the graphite structure of iron and hardens and strengthens it; but, in sharp contrast to nickel, chromium increases chilling tendency and promotes the formation of free carbide. Chromium acts, therefore, in an opposite manner to nickel in this respect and tends to neutralize its chill restraining effect. Chromium, however, also acts to build up combined carbon in iron and this feature renders it useful in conjunction with nickel in castings of heavy section.

If nickel and chromium are added to iron in the proportions in which they mutually balance each other with respect to chill, the resulting alloy iron will have the same chilling tendency as the plain iron to which the alloys were added, and castings made from it will be as readily machinable as castings from the plain base iron. At the same time the refining, matrix-hardening and strengthening effects of both alloys will be conserved and reflected in the structure and properties of the casting. This offers the foundry industry a useful tool for filling occasional orders for high grade alloy castings without altering the composition of the regular iron.

Molybdenum is another alloying element sometimes used in conjunction with nickel to replace or supplement chromium. Molybdenum is helpful in improving strength and toughness. It increases the chilling tendency slightly but its effect is not nearly as pronounced as that of chromium in this respect.

High Strength = High Modulus Irons

The property of rigidity is a function of the modulus of elasticity of a material. The modulus of steel is a constant regardless of alloy content or heat treatment. The modulus of cast iron, however, is not constant but is a function of the amount, distribution and form of the graphite. The average gray iron with a tensile strength of 25,000 to 30,000 lbs. per sq. in. will show a modulus of 13-14,500,000 lbs. per sq. in., and if a higher value is required a stronger iron must be used. By alloying with nickel or with nickel and chromium or molybdenum together with appropriate adjustments of the base composition as discussed in the previous paragraphs, tensile strengths up to about 50,000 lbs. per sq. in. may be readily obtained, but it is sometimes desirable for certain components to employ iron of 50-60,000 lbs. or even higher, either for strength alone or to

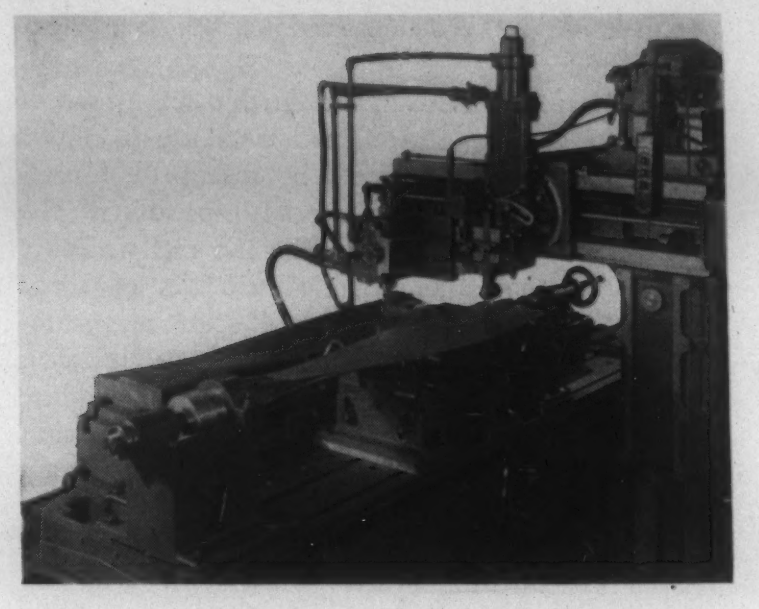


Fig. 9. Hydraulic shaper-planer forming propeller blade by means of a duplicating attachment. Nickel cast iron is used for the bed and table of the machine and also for the templates which guide the cutter. (Courtesy: Rockford Machine Tool Co.)

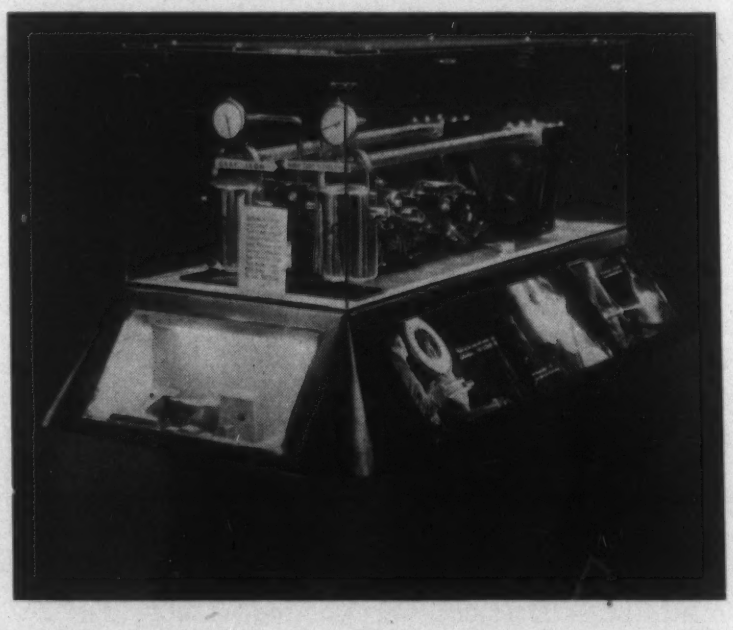


Fig. 10. Apparatus for demonstrating superior stiffness of nickel cast iron. Note position of arrows indicating relative deflections under equivalent loading.

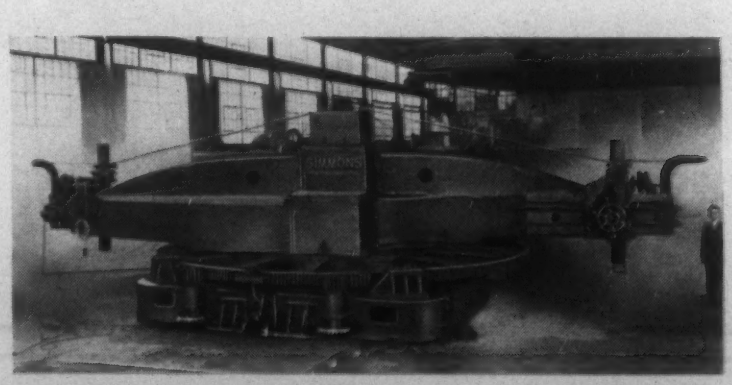


Fig. 11. Giant boring mill with important structural parts of nickel cast iron. The gears are made of cast nickel steel. Total weight of machine is over 185 tons. (Courtesy: Simmons Machine Tool Corp.)

obtain the 20-23,000,000 modulus which is associated with it.

It is possible to obtain machinable gray irons of strength exceeding 60,000, and even up to 80,000 lbs. per sq. in. if required, by means of a combination of alloying and special processing. The process consists of adding, while the melt is being tapped into the ladle, suitable quantities of alloys consisting of nickel, silicon, and sometimes chromium or molybdenum. This causes precipitation of fine, uniformly distributed particles of graphite in a matrix resembling alloy steel, thus producing exceptionally high strength castings with a gray fracture. Despite their very high strength, these irons exhibit a three fold increase over ordinary gray iron in resistance to impact.

Iron produced by this method is called "Ni-Tensyliron." Many foundries are producing Ni-Tensyliron to meet minimum tensile strength specifications of 50,000 and 60,000 lbs. per sq. in., and some are producing it regularly with a tensile strength of more than 70,000 lbs. per sq. in. These values are considerably higher than those obtainable by common melting practice.

The composition can vary over a wide range depending upon the size and thickness of the casting. The general range in composition follows:

	Per Cent
Total carbon	2.50 to 3.15
Manganese	0.50 to 0.90
Phosphorus	0.15 max.
Sulphur	0.12 max.
Silicon	1.20 to 2.75
Nickel	1.00 to 4.00
Chromium	0.00 to 0.50
Molybdenum	0.00 to 0.75

Heat Treatment of Cast Iron

Although many iron castings are used as they come from the mold without further thermal treatment, heat treatment of cast iron is not unusual. As in the case of steel, these treatments are varied according to the object in view, but they generally fall within four classifications: Annealing for softening, stress relieving or artificial "seasoning," flame hardening for surface wear resistance, and quenching and tempering. These will be discussed separately.

Quenched and Tempered Cast Iron

Added strength and wear resistance for machine tool parts subject to sliding contact, such as slides, guides and cams, can be secured in cast irons of suitable composition by a quench and temper heat treatment precisely as is done with steel. The only essential difference between gray cast iron and steel is the presence of graphite. Hence, the two materials should respond similarly to liquid quenching.

In steel the carbon present is all in the combined condition and exerts a powerful effect on the degree of hardness imparted by a quench. In gray iron, on the other hand, only the combined portion of the total carbon is effective. In ordinary gray iron the combined carbon content may vary all the way from 0.10 to 0.90 per cent in a single casting with consequent erratic response to quenching. Therefore, if heat treatment is to be worth the trouble and expense, it is necessary to secure a uniform high combined carbon content (0.60 to 0.80%) throughout the section or sections. The casting should also possess fine distribution of graphite with complete freedom from massive carbides or carbide clusters. The easiest way to obtain a uniform and fully pearlitic matrix which will respond well to liquid quenching is to add nickel, or balanced ratios of nickel-chromium or nickel-molybdenum, to a properly adjusted base mixture.

Just as in the case of steel, nickel reduces the thermal critical ranges of cast iron and also lowers the critical cooling speed. Both of these effects further facilitate the handling of the material in this type of heat treatment by lowering the necessary quenching temperature and by promoting a more effective penetration of the quench. The latter characteristic allows the use of milder quenching media and insures satisfactory response in heavy sections.

A manufacturer of a large multi-spindle drilling machine, finding it desirable to increase the hardness of column guides to promote lasting accuracy through improved wear resistance, achieved this end through the use of a heat-treated high test nickel-chromium iron. By this means he obtained a hardness comparable to that of heat-treated steel together with much better wear resistance at lower cost. The application was later extended to drill head spindle bodies and sleeves, saddles, swivels, tool guides, tool head guides and brackets. The composition of this iron is approximately as follows:

	Per Cent
Total carbon	2.75
Silicon	2.40
Manganese	0.70
Nickel	1.50
Chromium	0.50

As cast, this iron possesses a Brinell hardness of about 240 and a tensile strength of about 58,000 lbs. per sq. in. Quenching from 1550 to 1650 deg. F. into oil or water, depending on the section, followed by tempering at 850 to 950 deg. F. increases hardness to about 321 and tensile strength to over 80,000 lbs. per sq. in. The iron is found to be machinable at hardnesses as high as 340, yielding an exceptionally fine finish.

Annealing

The function of annealing is to decompose combined carbon and perceptibly soften the iron. Obvi-

ously such a treatment requires a temperature above the graphitizing point, usually 1450 to 1650 deg. F. depending on the degree of softening required and the intensity of the chill. Ordinarily annealing is a remedial measure aimed to restore machinability in chilled areas, which will be in the thinner sections or at edges. Obviously the annealing treatment can not be localized at these regions with the result that portions which are not chilled are depreciated in physical properties. It is much better practice to control chill by proper selection of alloy content and so avoid the necessity for this unsatisfactory reclaiming treatment. In addition to its deleterious effect on the non-chilled regions annealing not uncommonly introduces excessive warpage in castings which, due to shape and weight, can not be properly supported in the furnace. In fact, the authors have seen castings subjected to this treatment which warped so badly they had to be scrapped because machining tolerances were exceeded by distortion.

Stress Relieving

Stress relieving, or artificial seasoning, is a relatively low temperature annealing treatment designed to eliminate stresses set up by the cooling of the casting in the mold. The treatment insures stability during the subsequent machining and in service, minimizing any danger of gradual dimensional changes as a result of internal stress. The treatment is particularly desirable in connection with components of precision equipment where any appreciable distortion would be fatal. In some cases large castings, such as lathe beds, are seasoned by storing them for several months at atmospheric temperature.

The proper temperature for stress relieving varies according to the composition and structure of the casting, but should be carried out at the maximum temperature which will not injure the mechanical properties of the iron; usually somewhere between 900 and 1100 deg. F. Nickel alloy irons will withstand the higher temperature end of the range due to the stabilizing effect of the alloy content on the combined carbon. This stabilizing effect, as earlier pointed out, also reduces the intensity of casting stresses, thus further simplifying the treatment, even to the extent, in some cases, of entirely eliminating the need for it.

Castings should be cooled from the stress relieving anneal in the furnace. In some plants it is the practice to repeat the heating and cooling cycle to insure complete removal of all internal stresses.

Flame Hardening Cast Iron

The flame hardening process is a recently developed method by which selective hardening of wearing areas may be accomplished on parts which are too massive to heat treat easily in their entirety. As ordinarily carried out, the areas to be hardened are progressively heated by especially designed oxy-acetylene torches equipped with a series of water jets which follow immediately behind the burner tip, thus effectually quenching the heated metal.

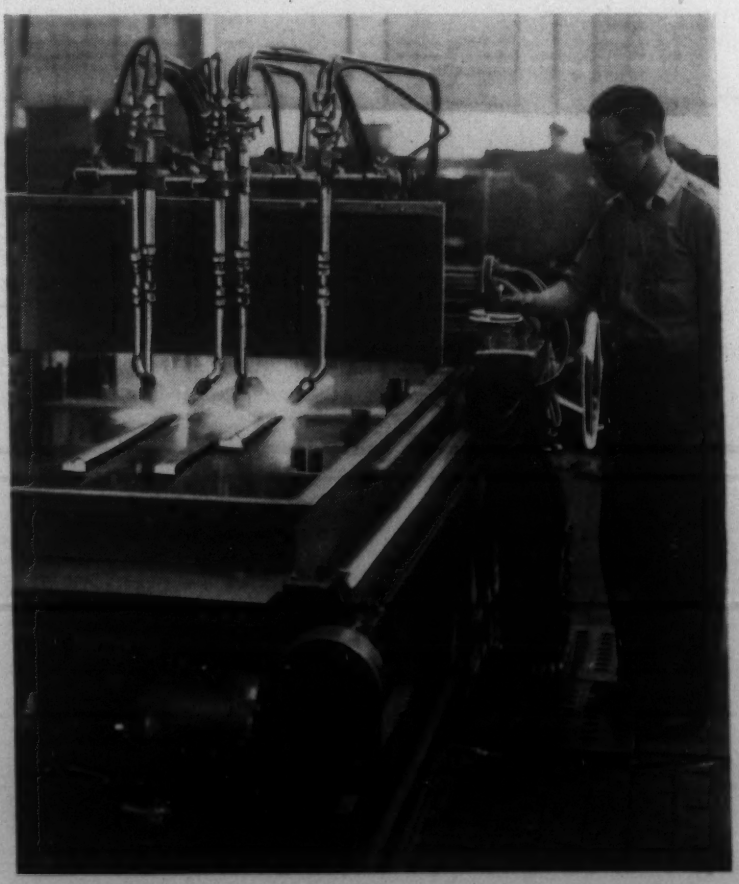
At first applied to steel, the possibilities of the process for hardening the wearing parts of heavy machine tool iron castings, such as lathe beds, were soon recognized. It was found that irons, suitably alloyed in accordance with the remarks in the quenching and tempering section above, would respond satisfactorily and the process is now in successful operation in several plants. Fig. 12 shows the method of hardening lathe ways used by one prominent manufacturer. The lathe bed is immersed in a tank of water to a point just below the ways and a motor driven mechanism draws the multiple heating and quenching unit over the ways at a proper uniform speed. Only one pass is required.

A nickel-chromium iron is used in this case not only to insure a good response to the quenching operation but to obtain good machinability and soundness in the whole casting. The as cast Brinell hardness of 225 to 240 is raised to over 500 on the ways by the flame hardening treatment. Some of these flame hardened beds have been in service nearly two years with complete satisfaction.

Finish

Since the redesigning of machine tools for the heavier demands now made on them has frequently been accomplished with little or no increase in the area of contact surfaces of reciprocating parts subjected to sliding contact, unit pressures are generally

Fig. 12. Flame hardening equipment in operation on nickel iron lathe ways. (Courtesy: Monarch Machine Tool Co.)



higher. This fact has led to a tendency to more refined finishes on such areas in accordance with the commonly held belief that wear and galling resistance increases continuously with improvement in smoothness and flatness of the mating surfaces.

Many designers are now of the opinion, however, that this idea can be carried too far and that such expedients as grinding of the wearing surfaces tend to defeat the purpose in view. Some even go so far as to hold that, assuming a proper mechanical fit, milled or planed surfaces will stand up far longer under severe conditions than either scraped or ground surfaces. They base this belief on the results of comparative tests and offer as an explanation the hypothesis that the low spots in the "rougher" finishes serve as reservoirs for the retention of oil and thus assure at least partial lubrication under conditions which would completely break down the oil film with the "smoother" finishes.

Machine Tool Applications of Nickel Cast Iron

It has been indicated that, due to extreme variations in size and service requirements, and differences in design among machine tools of various manufacture, a suitable iron composition must be selected individually for each application. Thus, while it is hardly possible to tabulate all the irons used for the various parts, it is believed that a useful purpose will be served by listing some representative compositions which are in actual commercial use for important components. This has been done in Table I. *(To be concluded)*

References

[1] L. F. Nenninger and W. A. Maddox. "Recent Developments in the Welding of Machine Tools." *Welding Journal*, New York, Vol. 7 (1938) October, page 36.

[2] Such a series of charts is contained in "The Properties of Quenched and Tempered Nickel Alloy Steels," published by the International Nickel Co., New York.

[3] T. E. Kihlgren. "Production and Properties of Age Hardenable 5 Per Cent Nickel Bronze Castings." *Trans.*, American Foundrymen's Assoc. Vol. 46 (1938) page 41.

TABLE I.—Representative Applications of Nickel Cast Irons in Machine Tool Construction.

Description of Part	Approximate Section Size [1]	Chief Service Requirements	Typical Chemical Composition					Tensile Strength in lb. per sq. in.	Brinell Hardness
			Total Carbon	Silicon	Nickel	Chromium	Molybdenum		
Bushing and bearings.....	L	Wear resistance with good machinability	3.50	1.80	1.50	0.30	[3]	33,000	200
	H	Wear resistance with good machinability	3.20	1.10	1.50	0.30	[3]	39,000	200
Beds, tables, saddles, slides, etc.	M	Resistance to wear and galling, soundness, good machinability	3.30	1.80	1.25	[2]	....	34,000	190
	H	Resistance to wear and galling, soundness, good machinability	3.20	1.10	1.50	[2]	....	40,000	210
Cams	M	Resistance to wear, good machinability	3.30	1.80	1.25	0.30	[3]	35,000	200 [4]
	H	Resistance to wear, fair machinability	3.10	1.60	2.00	0.60	[3]	46,000	240 [4]
Chuck bodies	H	Toughness, close grain in heavy sections, excellent machinability	3.30	1.80	1.50	[2]	[3]	35,000	190
Columns, guides, frames, etc...	M	Soundness, good machinability	3.20	1.50	1.50	0.60	....	40,000	230
High strength—Ni-Tensyliron	M	Strength, high elastic modulus, fair machinability	2.90	1.70	1.50	[2]	....	50,000	240
High strength—Ni-Tensyliron	H	Strength, high elastic modulus, fair machinability	2.80	1.50	1.50	....	....	55,000	240
Gears	M	Wear resistance, good machinability	3.30	1.50	1.25	....	....	38,000	200
	H	Wear resistance, soundness in heavy sections, fair machinability	3.20	1.10	2.00	0.30	[3]	48,000	240
High strength—Ni-Tensyliron	M	Strength, wear resistance, good impact resistance	3.00	1.50	2.00	....	0.65	60,000	240
Gear cases	L	Soundness, good machinability	3.30	2.10	1.00	....	....	33,000	210
Guides—see Columns.									
Hydraulic castings	L	Pressure tightness, wear resistance, good machinability	3.20	1.80	1.00	....	....	35,000	210
	M	Pressure tightness, wear resistance, good machinability	3.10	1.60	1.50	0.40	[3]	42,000	220
High strength—Ni-Tensyliron	M	Strength, pressure tightness, wear resistance, fair machinability	3.00	2.00	2.00	0.35	0.60	60,000	250
	H	Pressure tightness, wear resistance, good machinability	3.10	1.20	1.50	[2]	[3]	45,000	220
High strength—Ni-Tensyliron	H	Strength, pressure tightness, wear resistance, fair machinability	3.00	1.10	2.00	[2]	0.25	55,000	240
Saddles—see Beds.									
Slides—see Beds.									
Spindles	H	Wear resistance, good machinability	3.20	1.20	1.25	....	....	40,000	225
Tables—see Beds.									

[1] Section Thickness: L = Light—less than ¾ in.
M = Medium—between ½ and 2 in.
H = Heavy—over 1¾ in.

[2] For greater wear resistance and strength chromium may be added up to about one-third the indicated nickel content.

[3] Molybdenum may be added, with reciprocal reduction or elimination of chromium, where improvements in strength and toughness are desired.

[4] Hardness as cast. May be quenched and tempered to yield 450 Brinell if desired.

Dip Brazing

by FRANCIS G. JENKINS

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This article is "an excellent discussion on a topic on which it is otherwise difficult to get collected information," according to our editorial advisory board. It falls into the general class of a correlated abstract, though it is more than that.

The subject of dip brazing is an interesting one in the non-ferrous field. This article is valuable because it contains a review of correlated literature on the effects of addition elements to the brazing bath and excellent notes on brazing procedure. The author defines brazing as employing a thin film of copper or copper alloy to bond together overlapping surfaces by wetting and surface alloying; it is applicable only to parts that fit closely.—The Editor.

BRAZING EMPLOYS A THIN FILM of copper or copper alloy to bond together overlapping surfaces by wetting and surface alloying and is only applicable to parts that fit closely. This is as contrasted to fusion welding which refers to the joining of two metals by partial fusion, using a third metal as a filler and is usually applied to heavy sheet and plate stock. Brazing may be performed by a hand torch, though frequently it is done in a furnace or in a brazing pot and, occasionally, by electric heat from carbon resistors or by the carbon arc.

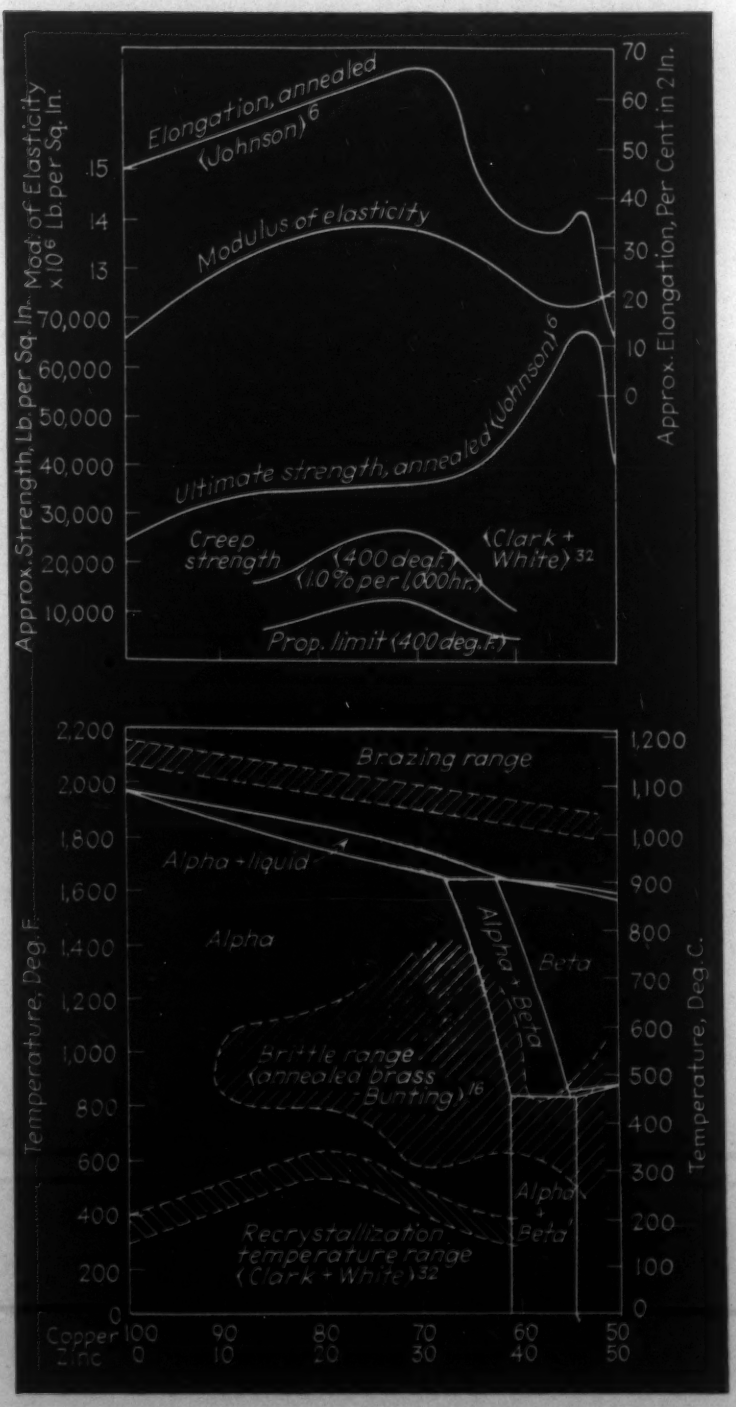
Where the quantity of work justifies it, the parts to be united are passed through an electric furnace in which a reducing atmosphere serves as a flux or are dipped in a brazing pot. In electric furnace brazing, the brazing metals applied during assembly in either solid or paste form, melt and flow into all joints by capillary attraction. Then, on transfer of the work to a controlled atmosphere cooling chamber, these alloys solidify, and the parts come out of the furnace with firm strong bonds and clean bright surfaces.

Furnace brazing, while successfully applied in many applications, does possess limitations that are not conveniently overcome. For example, it is generally acknowledged that the chromium in stainless irons renders the furnace brazing of stainless iron and steel quite difficult. The chromium oxide film surface is not reduced in ordinary furnace atmosphere and therefore the brazing material does not wet the metal.

Dip Brazing

The term dip brazing is applied to a process for joining ferrous metals with alloys of copper and zinc which consists, substantially, of dipping the parts to be brazed into a sufficient quantity of flux-covered molten-brazing material contained in a refractory crucible. Once the technique of the process is established, it is possible to achieve an order of economy, strength and reliability that cannot possibly be ob-

Fig. 1. Equilibrium diagram and cast properties of copper zinc alloys.


Mod. of Elasticity x 10⁶ Lb. per Sq. In.
Approx. Strength, Lb. per Sq. In.
Approx. Elongation, Per Cent in 2 In.
Elongation, annealed (Johnson) 6
Modulus of elasticity
Ultimate strength, annealed (Johnson) 6
Creep strength (400 deg. F.) (1.0% per 1,000 hr.)
(Clark + White) 32
Prop. limit (400 deg. F.)
Brazing range
Alpha + liquid
Alpha
Alpha + Beta
Beta
Brittle range (annealed brass (Bunting) 16
Recrystallization temperature range (Clark + White) 32
Temperature, Deg. F.
Temperature, Deg. C.
Copper
Zinc

tained by hand brazing methods.[15] For obvious reasons the method is applicable only to angle or end joints and not to straight joints.

Pot or dip brazing is used quite extensively in many industries as an important manufacturing process. It probably came into common use with the inception of the bicycle and has been widely employed in the motorcycle, automobile, and aircraft industries.[13] One of the most interesting applications is found in marine steam turbine construction, where it has for the last few years played an essential part in the production assembly of stainless iron, reaction turbine blading.

Dip Brazing Materials

Copper and copper-zinc alloys and in particular the 60-40 brasses are the metals employed for pot brazing because of their ease of brazing and their subsequent strength and ductility. At one time or another, a large variety of complex brasses have been used, all of which have indicated, but only indifferent, possibilities. Though not common, silver solders have been employed because of their low brazing temperature of approximately 1600 deg. F. and excellent strength and ductility.[35] Their high cost has prohibited their use, however, for most applications where cheaper alloys can be satisfactorily used.

COPPER: Although copper possesses flowing qualities superior to copper-zinc alloys and does not exhibit the pronounced hot shortness of the alpha brasses, on the other hand its strength is relatively low both at room and elevated temperatures and what is more important, its melting point is high. It has been the author's experience that this latter is a serious disadvantage for the difficulties encountered in production multiply rapidly with increasing melting points. It is necessary to carry out the brazing operations, when using copper, at a temperature of about 2100 deg. F. which among other things involves a rapid pot deterioration, not only expensive in itself but, in addition, effects production delays.

If copper were employed as a brazing medium, deoxidized, Lake copper would seem to be the preferable type. Lake copper differs from the electrolytic in that it contains small amounts of silver which raises the recrystallization temperature from approximately 400 deg. to 600 deg. F. and thus the creep strength in proportion. This latter property is of considerable importance in applications such as turbine blading involving elevated temperatures.

BRASSES: When zinc is added to copper in increasing amounts, the copper is somewhat strengthened, but its essential physical properties, low strength and high ductility are not materially altered until over 30 per cent zinc has been added (see Fig. 1). Above this amount the appearance of the beta constituent increases the strength of the alloy while the ductility becomes somewhat lower. The copper-zinc ratio of 57-43, approximately half alpha, half beta, produces in the annealed condition an excellent combination of high tensile strength and ductility, quite suitable for dip brazing material.

The alpha brasses (up to 39 per cent zinc and including the 90-10, 80-20 and 70-30 brasses) are also not considered to be as good as the alpha-beta brasses for brazing metal because of the greatly increased width of the brittle range in the alpha brass.[16, 25] (see Fig. 1) According to Bunting,[16] the brittle ranges exist in brass of composition varying from 90 per cent to 52 per cent copper. The range reaches a minimum at 57.5 per cent copper and, on further increase of copper through the high alpha brasses, the range extends upwards then narrows down and terminates in the neighborhood of 90 per cent. The influence of rapid cooling, incidentally, is to cause a general increase in the brittle range, due either to coring or to the production of increased quantities of beta.

The reason for stressing the importance of the magnitude of the brittle range is that one of the most important factors in the success of dip brazing is the ability of the brazed joint to withstand the effects of the thermal contraction of the metals involved. On cooling from the brazing temperature, or on subsequent expansion and contraction due to temperature changes, differentials in expansion characteristics may be so great as to break the brass away from the metal even though penetration has been obtained. Thus, in order to obtain a tight strong joint, it is necessary to have a filler brass that possesses excellent ductility at all temperatures. On this basis, the alpha-beta brasses, specifically because of their short brittle range as well as their excellent properties at room temperature, are favored as the fundamental medium for dip brazing. When dip brazing with brass of this composition, little or no space is required and the resultant joints are found to have all the normal strength of the steel components.

Alloying Elements

The effect of added elements and impurities, even in comparatively small quantities, on the physical properties and brazing characteristics of the optimum copper-zinc ratio of 57-43 may be very pronounced and of considerable importance. The modifying elements, which fall into two classifications, alloying elements and deoxidizers, may be specified, for the ultimate composition in the brazed joint, to the following ranges:

Desired:	Copper	Zinc	Iron	Manganese	Phosphorus
	57.0	38.0	2.0	2.0	0.05 max

Permissible:					
Copper	56-58	Tin	0.5 max.	Aluminum	None
Zinc	36-40	Silver		Lead	None
Iron	4.0 max.	Nickel	None	Silicon	None
Manganese	3.0 max.			Arsenic	None
Phosphorus	0.05 max.				

It seems likely that the use of metals other than iron and manganese in brazing brass is quite unwarranted since those others which might be used, tin, and aluminum, are of doubtful physical value. Furthermore, aluminum must be avoided particularly because of its film forming properties and consequent hindering of the brazing operation, while nickel, arsenic, lead and silicon are not recommended because of various deleterious effects.

IRON: Iron, in quantities up to 1.5 per cent, improves the hardness, strength, ductility, (see Fig. 2) and shock resisting properties of both alpha and alpha-beta brass. According to Ellis,[21] above this percentage the strength and hardness decrease while the elongation continues to increase. The indications appear to show that the beneficial action of iron on the physical properties is greater in the case of brasses in which the beta phase is in excess.

The influence of small percentages of iron in increasing the physical properties of copper is in part due to the iron in solution with its actual entrance into the copper lattice as well as to the key action exerted by the mechanical mixture of particles of an iron-rich phase with the brass. In both its soluble and insoluble state the effect on the tensile strength is less than might have been anticipated.

Iron in excess of the maximum high temperature solubility will form rather large and perhaps segregated masses of an iron rich constituent. Though fundamentally this does not improve the structure of the brass, it does not have any great embrittling effect.

Iron is credited, when present in small amounts, by Hanson and Ford,[17] also Cook and Miller,[25] with raising considerably the recrystallization temperature of copper. M. Hansen in discussion of Cook & Miller's paper states there is no doubt that the retardation of softening in brass containing iron, subsequent to the commencement of recrystallation, is due to precipitation hardening.

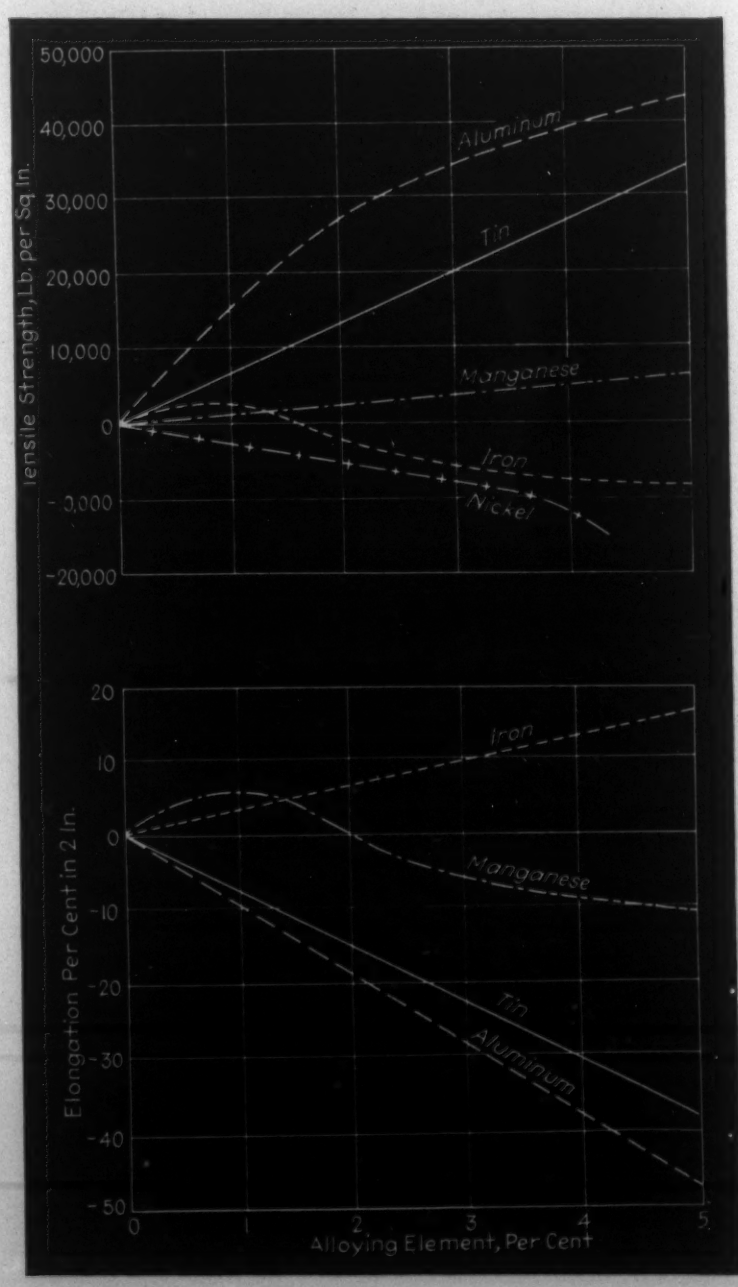
Beneficial properties are conferred by the presence of iron in brasses which improve their value as castings, for the iron appears to promote greater uniformity of size and shape of the alpha and beta crystals in a brass of complex structure while the grain size of the brass separating as the beta phase is reduced.[9]

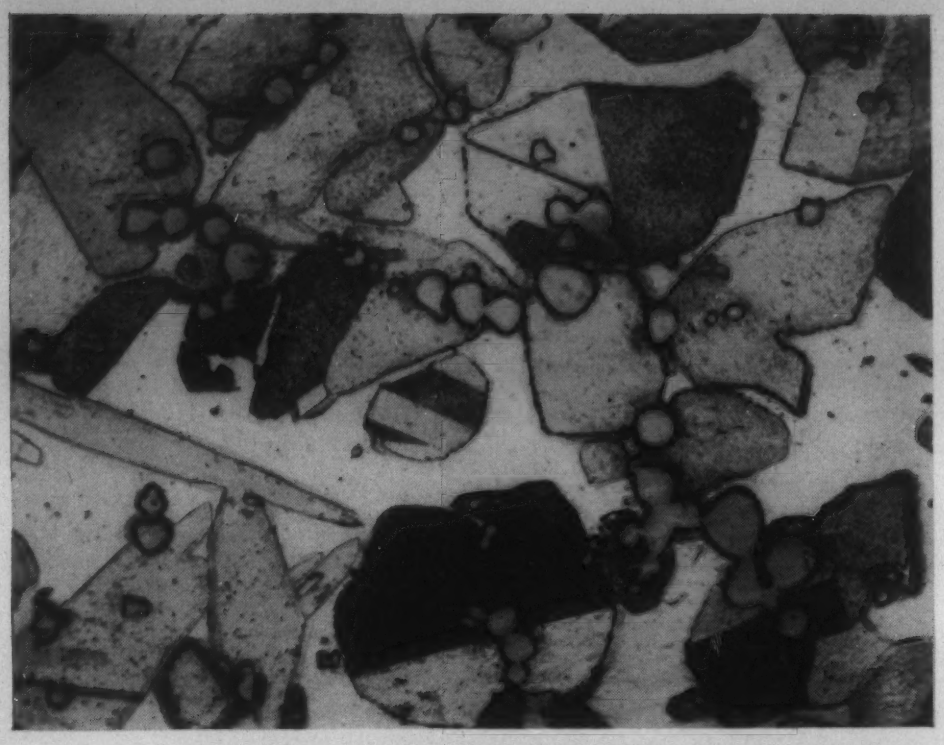
Though iron may be intentionally added in the foundry to a high strength brass such as manganese bronze, it is not added to the dip brazing brass since in the brazing of ferrous materials, the molten brass readily dissolves the iron from the brazed article. In fact the amount of iron absorbed in this manner can not be controlled and, because of the impossibility of eliminating it from solution, the brass bath must frequently be scrapped. A bath with 2 per cent iron represents a reasonable allowable maximum inasmuch as in the narrow spaced brazed joints, brass of this content will increase in iron and may average as high as 5 per cent, above which no possible advantage is obtained because of the previously mentioned gradual loss in strength.

Summarizing, approximately 2 per cent iron is desirable in these alloys, its special functions being (a) increase of recrystallization temperature (b) conferment of beneficial casting properties (c) reduction of grain size (d) conferment of ductility and toughness by reason of (c) and of iron in solution, as well as by the precipitation of minute particles of an iron rich phase.

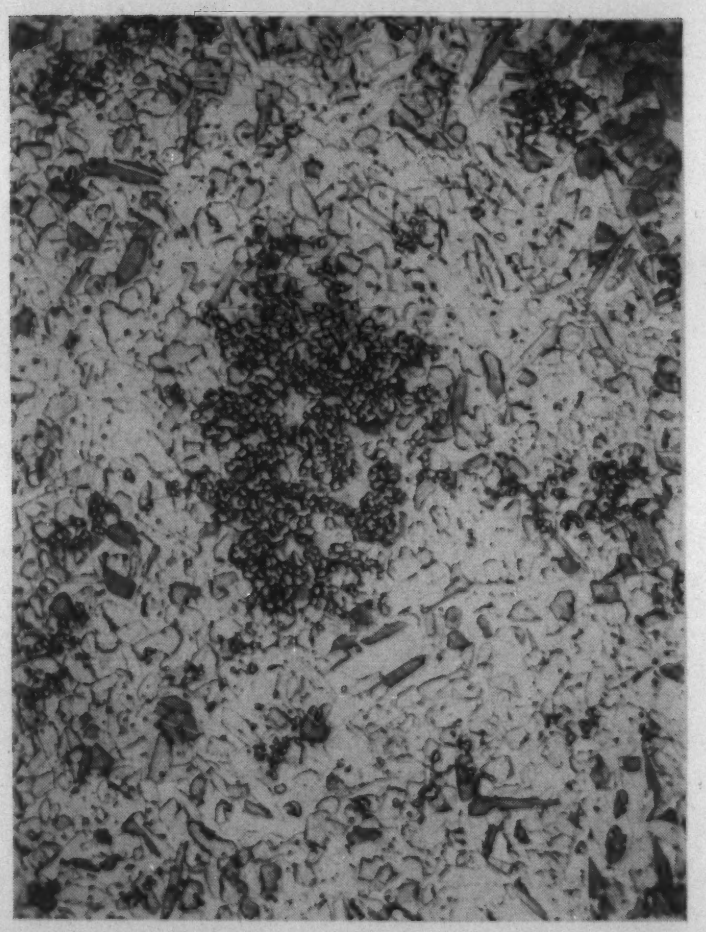
MANGANESE: Though manganese is a powerful deoxidizer easily fluxed, its primary use in brass is as an alloying element. As a deoxidizing agent, it reacts similarly in principle to phosphorus, although instead of the gaseous product of oxidation, the characteristic of phosphorus, the oxidation product of manganese, manganous oxide, is a fluid slag containing certain amounts of dissolved metals which, be-

Fig. 2. Effect of alloying elements on properties of 60-40 brass (Ellis).[21]





3a



3b

3c

cause of its comparatively low specific gravity, rises to the surface. The slag although quite fluid at the usual melting temperatures tends to form inclusions under normal conditions, particularly where in order to provide for a small excess of manganese in the alloys produced, more manganese is added than is necessary to deoxidize the metallic bath.

There is no reason why phosphorus cannot be used to deoxidize this brass and thus prevent the formation of a manganous oxide slag with consequent risk of inclusions. No ill effects need be feared as resulting from the presence of small amounts of phosphorus in the presence of manganese since phosphorus reduces the oxides before the manganese.[22]

Manganese dissolves readily in copper, up to approximately 30 per cent and to about the same extent in alpha and alpha-beta brass, producing a lower melting point, a slight hardening effect and increased tensile strength and, in additions of over 2 per cent, a reduced elongation. According to M. G. Corson,[20] the strength is thought to increase also because the manganese may exist in a state of submicroscopical distribution. Another reason accounting for the favor of manganese in brazing brass is that its presence undoubtedly increases the amount of iron which can be taken into solution and it has been shown that it raises the recrystallization temperature.

Summarizing, 2 per cent manganese is desirable in these alloys, its special functions being (a) increase in strength due to its entering into solid solution without any change in structure as well as to its possibly existing in a state of submicroscopical distribution especially in the beta phase (b) an ability to increase the amount of iron which can be taken into solution, and (c) increase in recrystallization temperature.

PHOSPHORUS: It is advisable to add approximately 0.05 per cent phosphorus because of its most favorable deoxidizing powers which will assist in the brazing operation. Though zinc itself possesses good deoxidizing properties, prosphorus reduces both copper and zinc oxide while the resulting phosphorus pentoxide (P_2O_5) vaporizes conveniently from the surface as a gas. Usually it is supplied as a copper-phosphorus alloy containing 10 to 15 per cent phosphorus in which it exists as the compound Cu_3P. Small amounts of phosphorus in brass are known in a general way to harden the alloy and raise the softening temperature.

TIN: The alpha and alpha plus beta solution of brass all dissolve a certain amount of tin varying from 0.5 to 2.0 per cent according to the composi-

Fig. 3. Photomicrographs of structures of a brazing brass of the following composition: 59 Cu, 37 Zn, 3 Fe, illustrating an average distribution as well as segregation of the iron-rich constituent. Etched with NH_4OH-H_2O_2.

tion. As regards the mechanical and physical properties, the addition of tin within the solubility limit in general raises the yield point, the ultimate and impact strengths, and decreases the ductility. When in excess of its solubility in copper and copper-zinc alloys, tin forms a brittle blue constituent known as delta. The presence of this delta constituent causes a rapidly increasing tensile strength and reduced elongation and impact strength.[18] Though usually uniformly distributed, it may segregate to the crystal boundaries producing an even more brittle condition. In view of the deleterious influence of tin on the structure and ductility of these alloys, it appears that it might well be eliminated.

SILVER: Silver is one of the most effective elements in raising the recrystallization temperature, and will, if anything, improve the brazing operation, though it will probably never be intentionally added on account of its expense.

NICKEL: Nickel is completely miscible in alpha and alpha-beta copper-zinc alloys and in a general way, it would appear that small percentages should reduce the true grain size and improve the tensile and elastic strengths. However, the addition of nickel to 60-40 brass is somewhat doubtful practice for it increases the melting point, requires deoxidizing and desulphurizing and if anything impairs the flowing properties.[11] According to Ellis,[21] nickel lowers the strength of brass when it replaces zinc; up to about 1 per cent, it increases the ductility slightly, if at all, and in quantities of more than 1 per cent, improves the ductility at a greater rate but apparently not to the same extent as does iron. The addition of nickel, because of its doubtful effects, is not recommended.

ALUMINUM: Of all the elements which may be encountered in 60-40 brass, there is no doubt that aluminum has the greatest influence upon strength. However, in spite of this, the presence of aluminum should be carefully guarded against because of its film forming tendencies and consequent hindering of the brazing operation. Aluminum also should be avoided because it increases the zone of red shortness, has a general embrittling effect, and, as a deoxidizer, phosphorus is preferred.

LEAD: The chief effect of the presence of lead is mechanical, and the elongation, tensile strength and impact strength are decreased. The presence of lead is to be avoided in brass in connection especially with apparatus working at high temperatures such as in steam turbine applications, for the lead is low melting and renders the brass hot short.

SILICON: Silicon is disqualified as a deoxidizer primarily because of formation of a slag similar to manganese with the consequent possibility of retaining silica inclusions. Other factors operating against the use of silicon have been the difficulty of introduction owing to its low specific gravity, and the fact that the mechanical properties of the ternary copper-zinc-silicon alloys are by no means outstanding.

ARSENIC: In alloys of the Muntz metal class, even very small quantities of arsenic have an injurious effect, reducing the ductility and resistance to impact of the hot-worked metal. The arsenide makes its appearance in the beta constituent, and with increasing quantities forms films which produce intercrystalline brittleness.[5]. The resulting fractures are coarsely crystalline; the coarseness and depth of color increasing with the arsenic content.

Metallographic Study

Metallographic study of 60-40 brazing brass (annealed at 1350 deg. F.) reveals a part acicular and part equiaxed precipitate of alpha (etches dark) in a matrix of the harder beta, together with a small amount of blue iron rich compound. The exact composition of the iron rich phase is not determined but every evidence indicates that it is a solid solution of iron and copper or iron, copper and zinc.

Cold worked alpha-beta brass will yield twinned alpha brass grains when annealed at a medium low temperature. Attention is called to the twinning in the photomicrographs of the brazing brass. This brass has been worked on cooling from the brazing temperature, probably by differentials in the expansion coefficients of the brass and the steel; and subsequent annealing has produced the twins.

Brazing Procedure

Dip brazing is accomplished in a graphite crucible, heated in a melting furnace, fired with gas or heated by electric induction. The brass is made by melting down the desired composition in bar form or by first melting the copper, then adding a layer of flux, (borax), dissolving the manganese and finally adding preheated but solid zinc. Incidentally, since molten brass gives off zinc during the entire brazing cycle and up to the time of solidification, frequent analysis must be made of the brass and sufficient zinc added to retain the specified composition.

The zinc helps to maintain the melt in a deoxidized condition by deoxidizing the copper, the zinc oxide floating off in the borax covering. After suitable intervals, the melt is deoxidized with phosphorus which is vigorously stirred in with a graphite rod. Using borax over the molten brass not only reduces the zinc loss due to volatilization to a minimum but also provides a covering which prevents access of air to the melt.

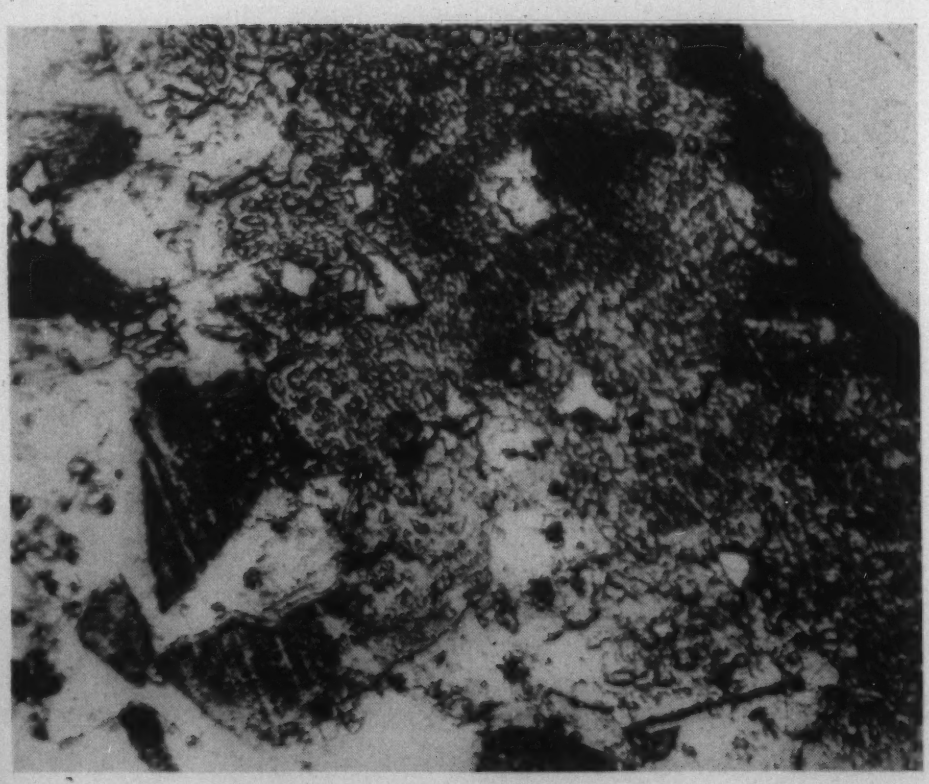
The brass is heated to the lowest temperature at which it will readily flow, since overheating is not only more expensive but will cause increased pot deterioration as well as excessive fuming of zinc oxide producing inferior weld metal. The optimum temperature for the dip brazing with the 60-40 mixture is found to be approximately 1900 deg. F. Below

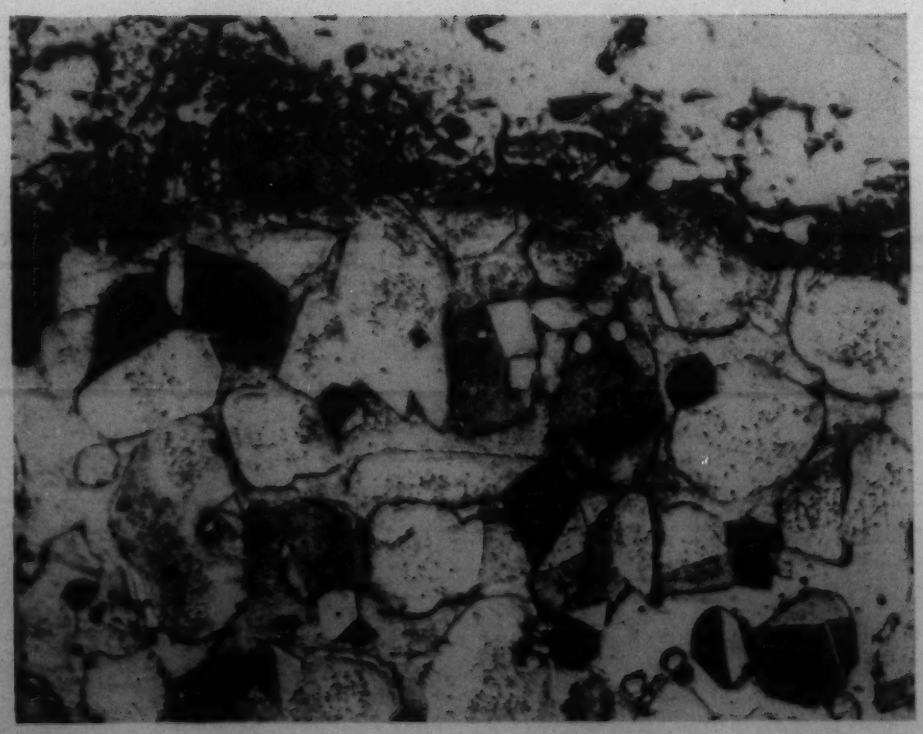
this, the temperature is too low to satisfactorily braze steel, for the fluidity of brass and flux is too poor to prevent the formation of flux inclusions in the brazed joint, which of course must be avoided as they may be a source of failure.

In the airplane and automobile industry, fittings are manufactured very largely by being built up of sheet metal stampings which consist of a large number of various pieces of steel fastened together by either spot-welding, riveting or tack welding with an acetylene torch. It is essential that they be securely fastened in order that the rapid expansion caused by immersion in the molten spelter during the brazing operation will not loosen any of the various parts.[13]

In general, the pieces to be brazed are cleaned, pre-fluxed, assembled with proper clearance, pre-heated, dip brazed, heat treated (if base material warrants it) and finally recleaned. Reaction turbine blading segments are joined by dip brazing, simultaneously, a number of stainless iron blades spaced with packing pieces. The blades and packing are initially clamped together in a suitable jig in their desired relative positions and are secured by arc welding along the bottom. The dipping mechanism is similar to that used by Parsons[33] where the segments are suspended on a hook attached to a long arm. The position of the arm is regulated by a cam which is motor driven so that the roots of the segment successively dip into the borax and brass and are detained in both mediums for suitable intervals.

Fig. 4. Photomicrographs of boundary of brazing brass and 13 per cent chromium-iron illustrating depths of iron-rich alloy. Etched with NH_4OH-H_2O_2. 500 X.





Precleaning

It is essential that the parts, where it is desired to effect adherence, are perfectly clean and free from any foreign matter that might interfere with or prevent melting and capillary flow. With the usual ferrous and non-ferrous metals such as steel, copper and nickel, it is necessary only that the base metal be free from oil, grease or scale. These materials may be cleaned by emery, grinding, buffing, wire brushing or by washing with carbon tetrachloride.

However, with stainless steels a thin tenacious coating of oxide is retained on the surface, even despite thorough mechanical cleaning. The black oxide film on stainless, consisting chiefly of chromium oxide together with smaller amounts of iron oxide, manganese oxide and silica, requires for removal a severe pickling or solvent cleaning. Parsons cleans stainless iron turbine blading by heating in hot 50-50 hydrochloric acid and then dipping in concentrated nitric acid and washing in water.[33] Another very good practice is to clean the blading by electrolytic pickling and then to place in carbon tetrachloride until ready for assembling.

The electrolytic pickling is more rapid and better than still pickling, requiring in most cases from 1-3 minutes for completion, whereas still pickling may require 10 to 15 minutes for the same type of scale.[36] Much less acid is consumed in electro-pickling than still pickling and the savings in iron and acid usually outweigh the added cost of power. Furthermore, this method separates the scale layer from the basic metal surface without damage to it, regardless of the variation in thickness of the scale.

Clearance

A brazed assembly should be fabricated in such a manner that the joints to be brazed fit closely together. In fact the strength of the brazed joint is not affected as much by the composition of the brazing mixture as by the amount of clearance. The brass fills the joints by capillary action wetting the clean

surfaces of the metals to be joined and the surface alloying thereto.

The adherence of the brass to the base metal is thought to be the result of three effects, tinning, alloying and inter-granular penetration. Void spots or gaps are always difficult and many times impossible to seal due to the dependence on capillary attraction for drawing the molten metal into the joints. The smaller the capillary, the greater the attraction and the stronger is the joint, the srength increasing down to clearances of 0.003 in. The optimum clearance between the surfaces to be joined will vary according to the alloy used and the metals joined.

Preheating

The pieces are pre-fluxed before assembly to prevent oxidation of the cleaned surface during pre-heating. Pre-heating to a dull red just before dip brazing in a pre-heating oven is found desirable, but a higher temperature or continued heating should be avoided because of possible oxidation of the surfaces to be brazed despite careful pre-fluxing. A higher pre-heating temperature furthermore is unnecessary, as sufficient pre-heating is provided by holding in the flux carried over the brass bath. Depending on their size, stainless iron blade segments are held in the borax covering, 2 to 10 minutes, in order to thoroughly preheat as well as to flux.

The specimens must be given sufficient time in the brass in order to reach the temperature of the brass as very little brazing takes place until the steel arrives at that temperature. The brass simply freezes around the specimens until the heat from the molten mass sufficiently penetrates the specimen.

Fluxes

In dip-brazing, the flux is in the form of a bath from 2 to 4 in. thick, floating on top of the molten brazing mixture and is a very important factor in successful brazing, especially in the case of stainless irons. In using a flux, we have a two-fold purpose in mind: (1) to protect the metal from oxidation and to dissolve oxide, (2) to improve the fluidity of the molten metal by removing non-metallic impurities.

The stainless steel class of metals, with their refractory chromium oxide film are quite highly resistant to chemical action requiring a rather active chemical to properly react as a flux. A number of fluxes have been proposed for surface coverings on the brass including borax ($Na_2B_4O_7$), boric acid (H_3BO_3),[33] potassium metaborate and others.

As a flux, borax[12,33] is the most active, removing the oxide much more quickly than other fluxes and insuring a better joint. Commercial powdered borax contains approximately 47 per cent of water of crystallization which causes a bubbling action during heating. This agitation is not serious in most soldering operations but can be avoided by using fused borax. Ordinary borax is widely used also because of its valuable properties in improving the fluidity of the molten metal, though it may be somewhat difficult to clean from the segments on cooling after brazing.

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Fatigue Problems in the Electrical Industry

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THE FATIGUE PROBLEMS of the electrical apparatus manufacturing industry are characterized by unusual variety. The company with which the writer is associated manufactures slightly more than 8000 products classified by type, which can be considered typical of this kind of industry. Furthermore, the nature of the products is such as to present numerous fatigue problems, since many rotating and vibrating parts are involved. It is proposed to review briefly a few selected examples of service fatigue failure and

Fig. 1. Fracture surface of generator rotor end forging.

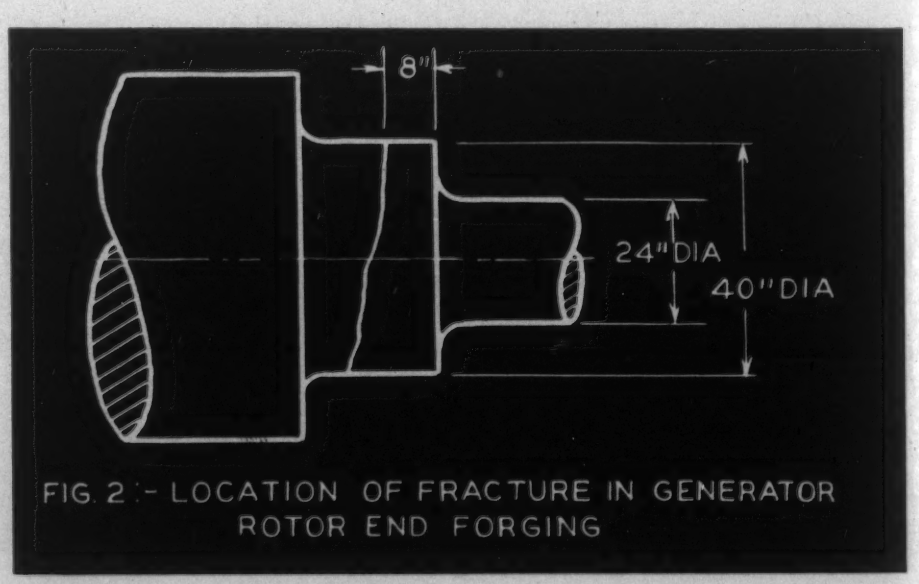

FIG. 2 :- LOCATION OF FRACTURE IN GENERATOR ROTOR END FORGING

Fig. 2. Location of fracture in generator rotor end forging.

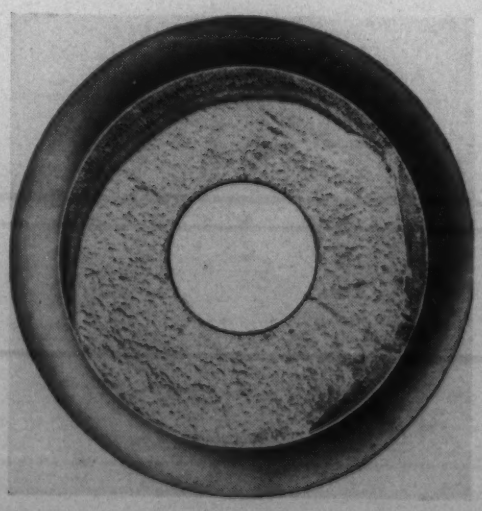

Fig. 3. Shaft fracture resulting from a flaw in forging.

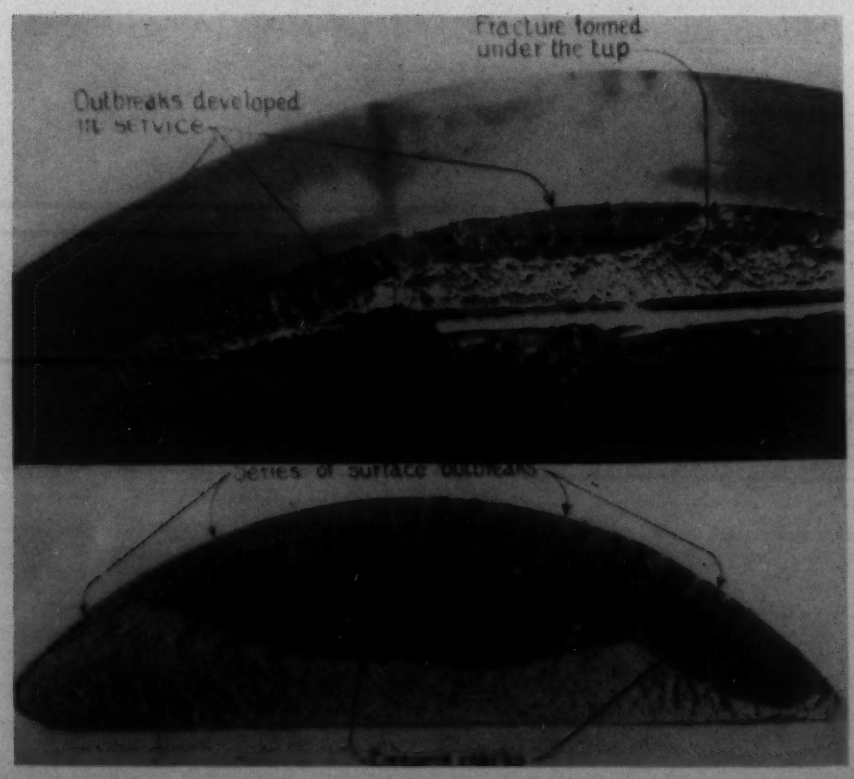

Fig. 4. Failure of engine shaft.

to point out characteristic features in each case. Corrective solutions are indicated in a number of cases.

In Fig. 1 is shown the appearance of a fatigue fracture of a large generator rotor end forging. The location of the fracture is sketched in Fig. 2. The calculated stress was very low and the external conditions were such that stress concentration conditions would not be expected at the section where failure occurred. In this connection, we observe that the circumferential rings on Fig. 1 are unusual and are not found in laboratory fatigue tests[1]. These apparently are due to defects or thermal stresses associated with manufacture of the forging, since there are no other likely reasons for their appearance.

There are a few similar cases in the literature. In Fig. 3 is shown a rough machined forging[2] which, when being transported by a crane, was bumped to an extent sufficient to cause the fracture shown. One not knowing the facts might easily mistake this for a fatigue failure. The main point of interest in this connection, however, is the presence of unnoticed defects in the rough machined forging. In Fig. 4 are shown defects in a steam engine crankshaft[3]. In Fig. 5 is shown a car axle journal which had presumably run hot[4]. This is not intended to illustrate a defective forging but is of interest in showing a possible connection with initial damage caused by thermal stresses.

Experiences of the kind discussed in the foregoing have led to improved annealing and forging practice on the part of the supplier and very careful inspection of completed forgings by both supplier and buyer. Optical and magnetic apparatus have been helpful in this connection.

An example of repeated torsion failure is found in Fig. 6 showing the typical helical path following the direction of normal stress. The shaft (normally stressed at 200 lbs per sq. in. was part of a large motor-generator set which unfortunately operated near resonance. A flexible coupling completely corrected all sets of this particular design by lowering the natural frequency and thus "detuning" the system.

Another interesting example of repeated torsion failure (Fig. 7) is the fractured shaft of a Diesel driven generator. Here, because of the small flange fillet, part of the failure was localized so that a number of helical cracks joined with a resultant saw tooth appearance.

Fig. 5. Failure of railway axle journal.

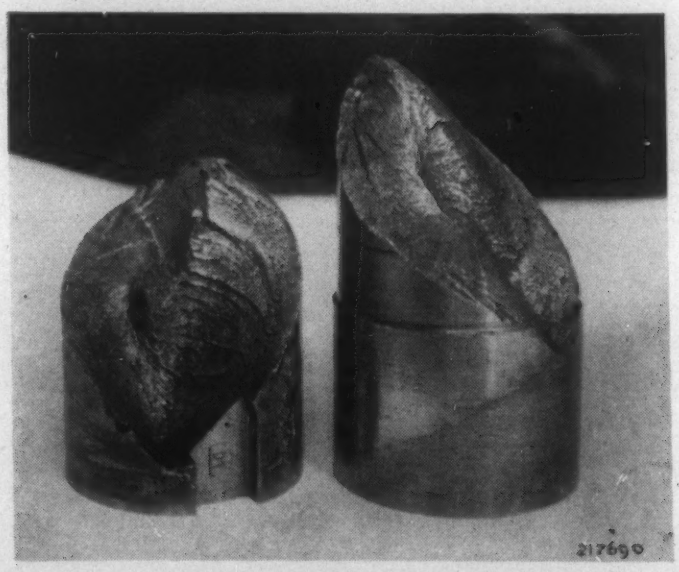

Fig. 6. Failure of motor generator shaft due to torsional resonance.

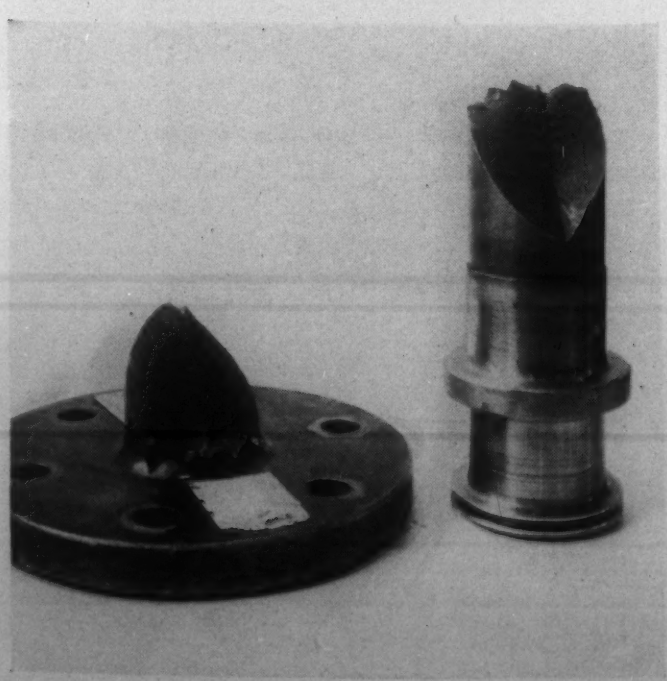

Fig. 7. Failure of diesel driven generator shaft.

Fig. 8. Failure of helical spring in marine application.

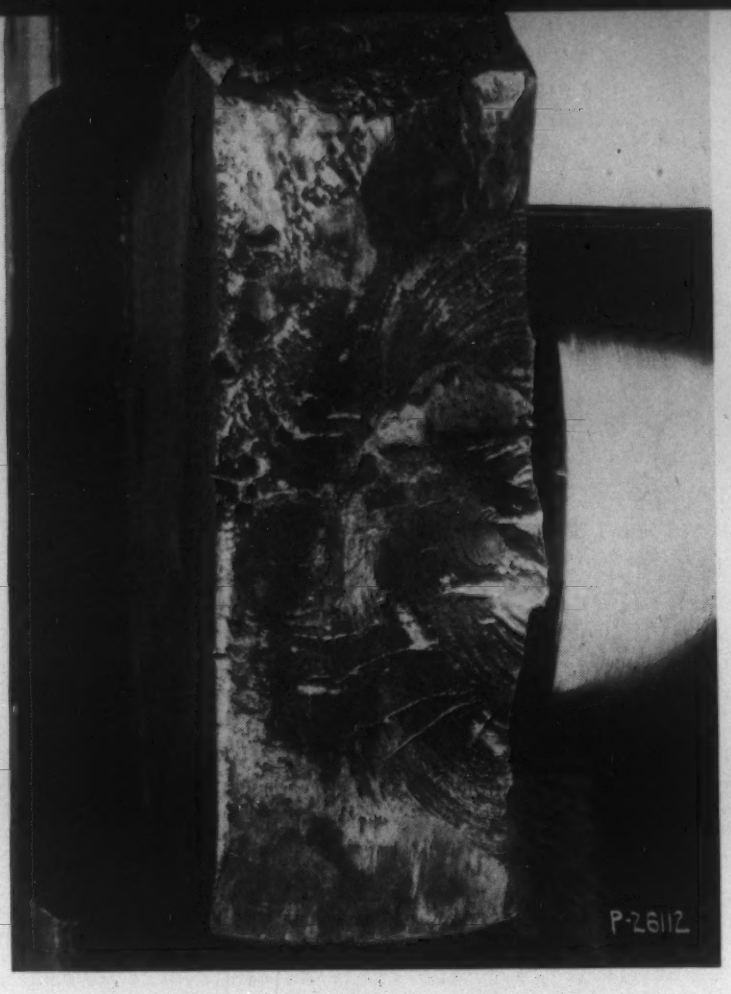

Fig. 9. Failure of diesel engine crankshaft.

Fig. 10. Failure of diesel engine crankshaft.

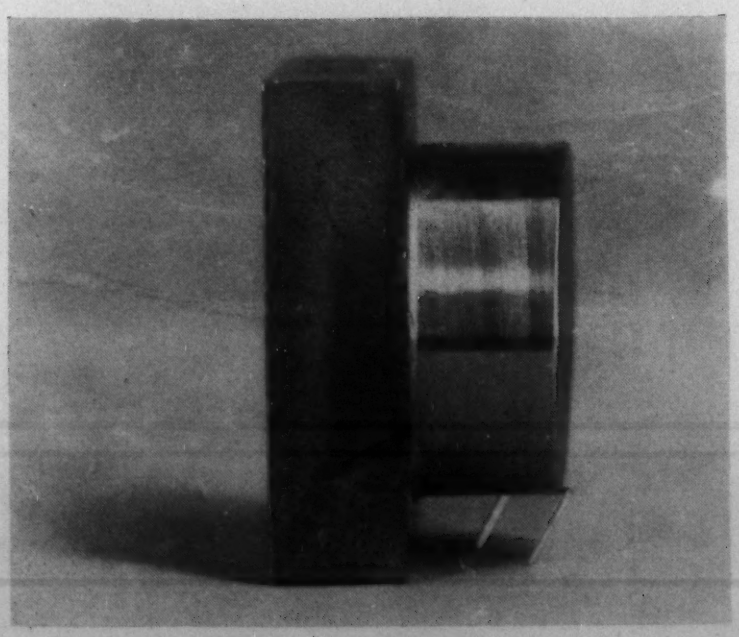

Fig. 11. Failure of crankshaft model in bending.

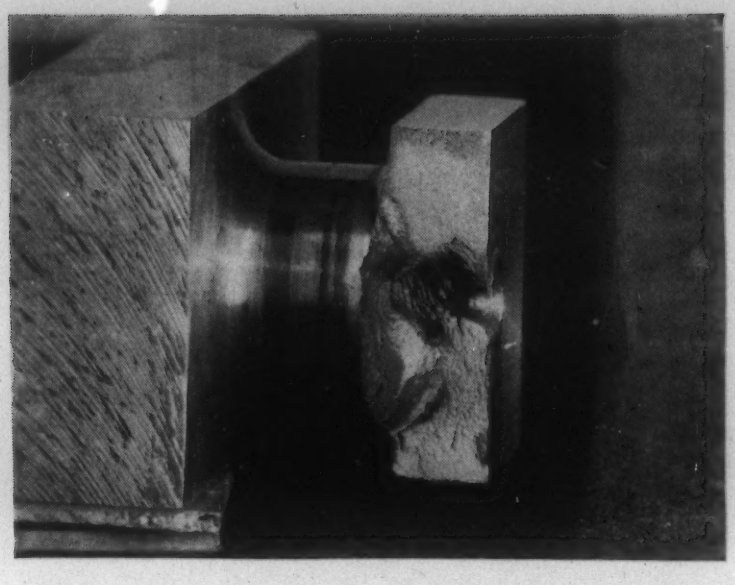

Fig. 12. Failure of crankshaft model in torsion.

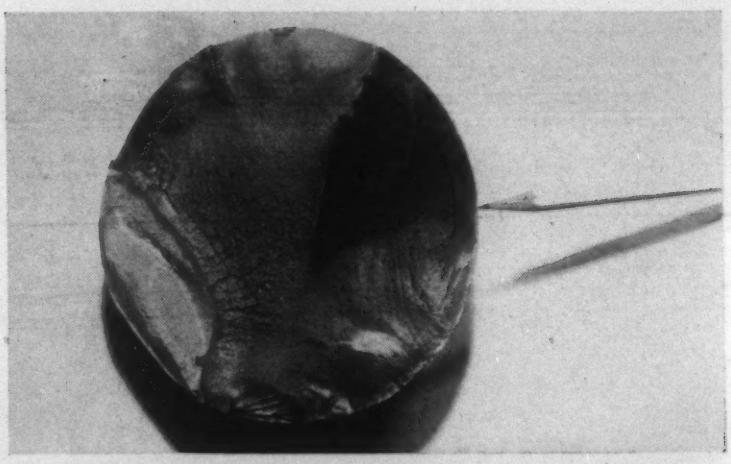

Fig. 13. Failure of oilwell pump crankshaft.

Fig. 14. Failure of streetcar motor shaft.

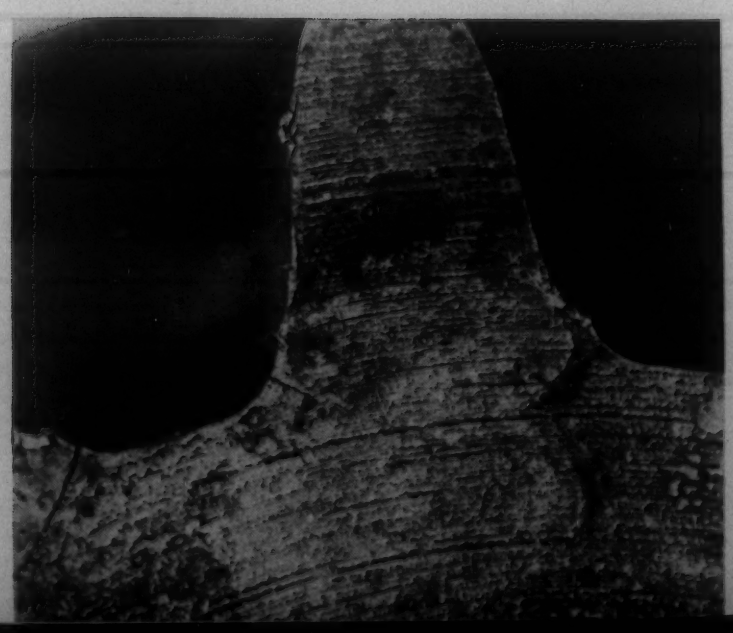

Fig. 15. Failure of fatigue cracks in gear teeth.

Fig. 16. Failure of tooth in the same gear as shown in Fig. 16.

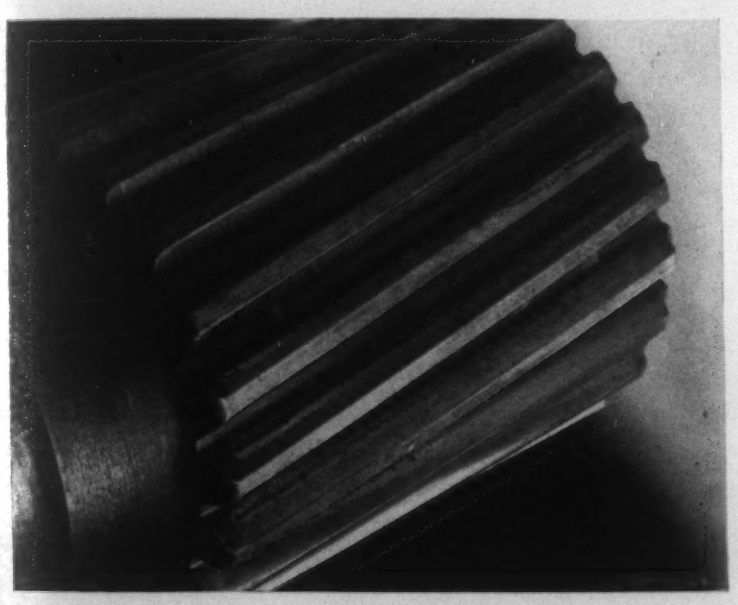

Fig. 17. Pitting of gear teeth.

A further example of repeated torsion failure is illustrated by the characteristic appearance of a helical spring failure shown in Fig. 8. Failure starts from the inside as theory predicts and again follows the direction of normal stress.

Two types of failure experienced in Diesel engine crankshafts (Figs. 9 and 10) led to model tests resulting in the bending fatigue failure across the cheek (Fig. 11) and the torsion fatigue failure in the journal fillet (Fig. 12). These criteria are of value in determining possible causes of trouble, for example whether due to misalignment or an inoperative torsional vibration damper.

Incidentally, it is of interest to note that, if the fillet of a repeated torsion specimen is made small enough, failure can apparently be localized therein. The ratio of r/d (fillet radius / shaft diameter) is the main criterion theoretically. In Fig. 7 this ratio is 0.12 and in Figs. 10 and 12 is 0.05, which suggests a limiting value in the neighborhood of 1/10.

In Fig. 13 is shown the fractured surface of an oil well pump crankshaft which was subjected to combined torsion and bending. Failure occurred at a place where a roller bearing was fitted to the shaft. This brings up the subject of fatigue of fitted members on which a considerable literature exists.[5] It turns out that the presence of a fitted member can reduce the fatigue strength of a shaft to one-half or one-third of its nominal value. To increase the strength in such a case, the shape of the fitted member may be altered in such a way as to relieve the high corner stress, or the shaft may be strengthened by cold-rolling. In the case of the oil well pump crankshaft the latter expedient was used with complete success.

Fatigue failure of an overhung pinion shaft of a street-car motor drive is shown in Fig. 14. The type of keyway illustrated is the so-called "profiled" type which is cut with an end mill. Tests[6] have shown that a considerable improvement is obtained by using the so-called "sled-runner" type.

In Figs. 15 and 16 are shown the fatigue failures of gear teeth due to beam action. It is of interest to note that the location and direction of the cracks check with the results of photoelastic studies. Failures of this type, i.e. as a beam, were more common with the relatively narrow teeth corresponding to low pressure angles which were in greater use formerly. The limiting condition with gear teeth having a pressure angle of 20 deg. or greater is in most cases determined by a different kind of fatigue failure, namely "pitting." Pitting has been described elsewhere[7] but may be briefly described as a failure due to repeated contact stress of lubricated surfaces. Improvement of "pitting limit" can be effected by higher hardness of materials, higher viscosity of lubricant, or better surface finish.

It is hoped that this brief summary will be of value to engineers in other industries in diagnosing and correcting troubles and also that it may suggest problems for investigation at university laboratories.

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Close Temperature Control in

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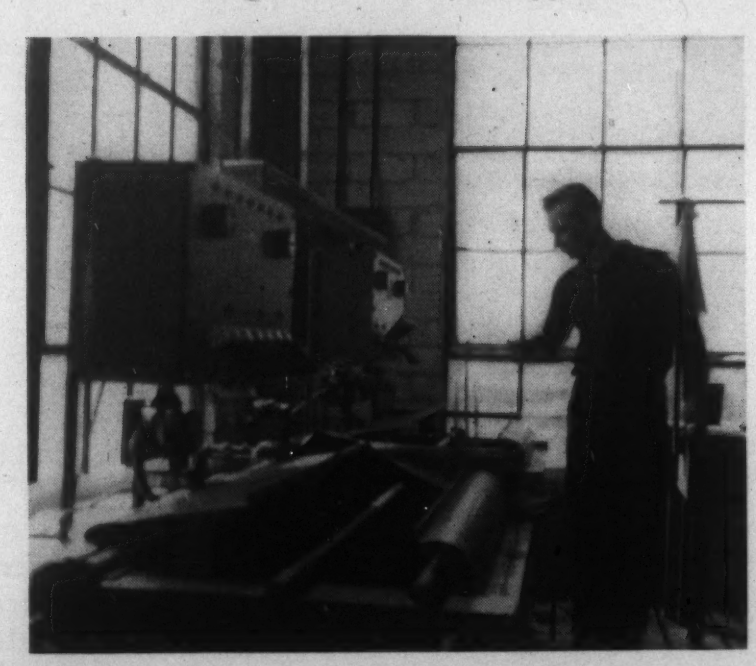
Metallurgical engineers need no reminder from us of the importance of careful control of temperature in melting, heating and heat treating—their constant interest in new or improved pyrometers testifies to that. But we wonder how many of them know that in one of their unit operations—chromium-plating—it is necessary to maintain bath temperatures to within plus or minus 2 deg. F. of the correct value.

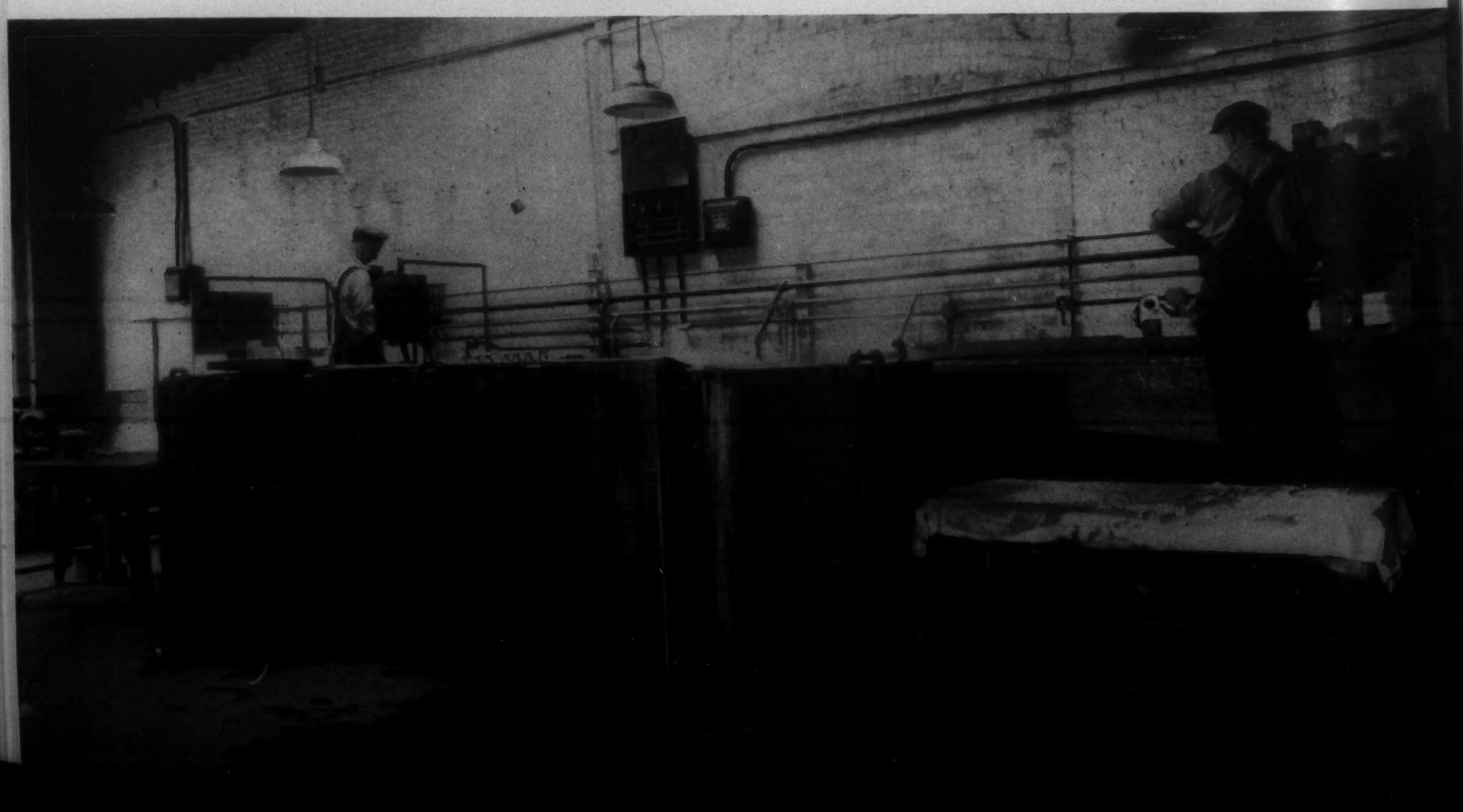
This article, which was submitted in a recent General Electric Co. industrial heating contest for electric power company salesmen, describes equipment used in a representative plating plant for maintaining the temperature of chromium-plating baths within these close limits, and gives operating and cost data.—The Editors.

Fig. 1. Some of the chromium-plating tanks to which the General Electric immersion heaters and temperature regulators were first applied.



THE IMPORTANCE OF MAINTAINING electroplating bath temperatures within as narrow a range as possible has always been recognized by platers and engineers concerned with such operations. Chromium-plating is particularly ticklish, and very often variations of more than 2 or 3 degrees F.

Fig. 2. Additional chromium tanks later outfitted with heaters and regulators.



Chromium Plating

may spoil, or at least complicate, an otherwise acceptable job. With engineers everywhere becoming increasingly conscious of "eye appeal" as an ultimate consideration in all metal working or finishing, the importance of finding simple, economical means of assuring perfect chromium deposits is obvious.

The author recently had occasion to study this problem at the plant of a representative electroplating company. For a good many years, their chromium-plating tanks had been heated with steam, and temperatures controlled with solenoid valves regulated by thermostats. This arrangement caused a temperature lag of approximately plus or minus 4 deg. F. When the temperature was maintained at 108 deg. F., an excellent plating job was accomplished, but if the temperature fell more than 2 deg. F., the work was spotted and plating uneven. If the temperature rose over 2 deg. F., the plating was gray and hard to buff. In this case, keeping the temperature at exactly 108 deg. F. had been found to save buffing and extra handling.

Use of Electric Heat

The possibilities of saving money on this operation by the use of electric heat appeared interesting, and it was decided to investigate the use of General Electric lead-covered electric immersion units in conjunction with close thermostatic control to keep even-temperature regulation. The size and cost of the units required were estimated, and an installation made in one of the small 300-gal. tanks, with the understanding that if this first installation proved satisfactory, units would be installed in the other tanks.

In figuring the size of unit needed for this 300-gal. tank, it was necessary, of course, to consider the room temperature, radiation losses, solution make-up, heat generated by chemical reaction in the solution, and heating-up time. The room temperature on winter mornings was sometimes as low as 50 deg. F., and the radiation loss from the tank was very small, with the exception of the open top of the tank, which was close to 4,090 B.t.u.'s per hr. The heat required to raise the temperature of the solution make-up was too small to make any difference in the size of the units, but the heat generated by chemical reaction was known to be considerable; thus the chromium tanks had been heated to temperature with steam in the mornings, and on days when the plating load was heavy the solution would maintain a temperature near 108 deg. F. with no auxiliary heat.

Heating-up time in the morning was another problem. As this plant was on a demand primary rate with off-peak hours at night, the current used between 10 P. M. and 7 A. M. would cost them eight mills per kw.-hr. Therefore, the cost of keeping this tank up to temperature all night would be the cost of current used to take care of radiation losses, which amounted to 13.5 kw.-hrs. during the 9 hrs. they did not operate, or 11 cents per night. This helped keep the initial cost of the installation low; large units were not needed for bringing the tank up to temperature in the morning.

It was calculated that a 6-kw. unit would raise the temperature of the solution enough for plating in about 4 hrs., if necessary, and a 6-kw., 460-volt, lead-covered General Electric immersion unit and thermostat were therefore ordered. The thermostat was used in conjunction with a relay, which, in turn, was actuated from a 110-volt supply and was capable of handling 40 amps. through contacts. The lead-covered unit was grounded to the tank and the tank was connected to water pipe for a good ground; the thermostat bulb was covered with a thin lead pipe and grounded to the tank, so no chemical reaction would take place. A good ground for both the unit and thermostat bulb is important, as it was found that the lead would be eaten away, especially that part of the unit at the surface of the solution.

Operating Economies

After the equipment was installed, this plating company had the production checked for one month and found the savings in the handling and buffing of chromium-plated automobile grilles to be around $200 per month. During this trial period the temperature of the tanks was held to plus or minus 2 deg. F., and the current consumption for this one 300-gal. tank was only 630 kw.-hrs. at a cost of $7.05 per month. The current consumption during the night periods was at least 405 kw.-hrs. more than the day consumption, because the electrochemical reaction furnished much of the heat during the day. The company was so satisfied with the operating costs and the savings obtained by using electric heat that they ordered 3 more 6-kw. units and thermostats to equip completely the rest of their chromium tanks. These were installed in the fall of 1935; the complete chromium-plating set-up is shown in Fig. 1.

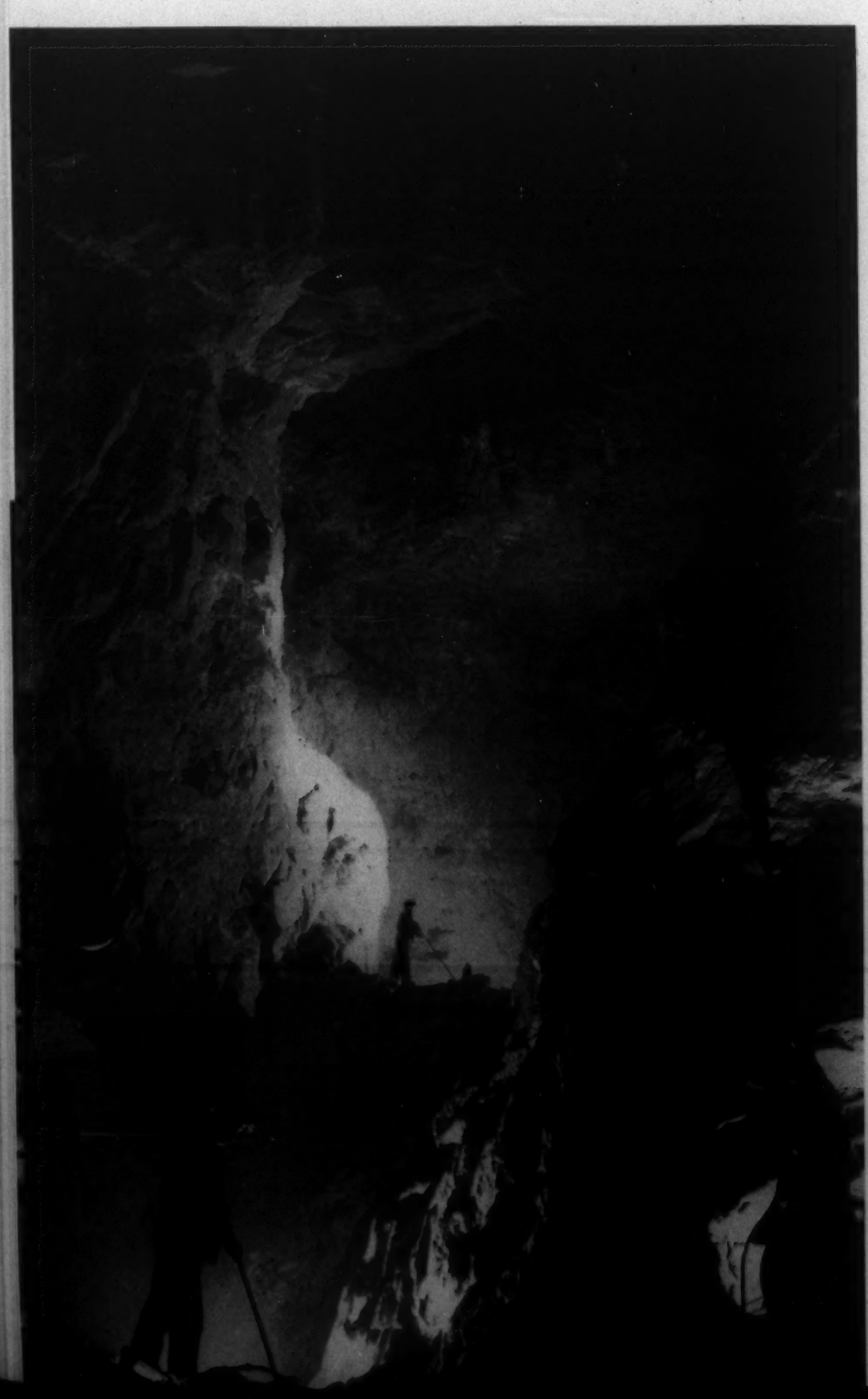
After these chromium tanks were used about one year, the company made an addition to the building and, along with the other equipment, installed 2 more 300-gal. tanks for chromium-plating and 2 more units and thermostats. These tanks are shown in Fig. 2.

Corrosion of Zinc

by E. A. ANDERSON and M. L. FULLER

Chief and Investigator, respectively,
Metal Section, Research Division,
The New Jersey Zinc Co., Palmerton, Pa.

Underground photograph of a stope in the Balmat mine (zinc ore) of the St. Joseph Lead Co., in St. Lawrence Co., N. Y. (Courtesy: St. Joseph Lead Co.)



So many of the commercial applications of zinc and high-zinc alloys depend on the corrosion resistance of the metal that industry will heartily welcome careful studies of zinc corrosion leading to improved resistance or to more efficient utilization of this important metal. First line of attack, of course, is the nature of the corrosion product in specific media, and in this article at least one outstanding and possibly unexpected conclusion is reached, namely, that the product of ordinary water corrosion and of indoor atmospheric corrosion of zinc is not zinc oxide, as has generally been supposed, but basic zinc carbonate. The results are based not only on X-ray diffraction and chemical analyses, but also on electron diffraction, the importance of which as a new tool for corrosion research has frequently been emphasized in this magazine.—The Editors.

THIS PAPER PRESENTS AN ACCOUNT of laboratory experiments resulting in an identification of the corrosion product of zinc under certain conditions of exposure and in observations on the mechanism of its formation. Atmospheric exposures under controlled humidity conditions and exposures by water immersion are included, particular attention being paid to the role of carbon dioxide in the corrosion process. Outdoor corrosion is not included in this paper but the laboratory results seem to be of sufficient fundamental importance to justify their publication at this time.

The principal method of examination employed in this investigation is that of electron diffraction. By this method surface corrosion films, too thin to be visible to the eye or to X-ray diffraction examination, may be detected and identified. X-ray diffraction and chemical analyses were used when the corrosion product was of sufficient bulk to utilize these methods.

Preliminary Work Leading to an Identification of the Corrosion Product

Early in the course of the use of the electron diffraction camera in this laboratory, it was observed that zinc surfaces are usually coated with a film yielding a characteristic diffraction pattern, the film being of sufficient thickness to prevent the photographing of the diffraction pattern of the underlying metallic zinc. To do this the overlying film need be only of the order of 10 to 20 atom layers deep, owing to the extremely low penetrating power of the electron beam.

It was found that the diffraction pattern of the film was similar to that originally obtained by W. L. Bragg and J. A. Darbyshire[1] from the skin that forms upon the surface of molten zinc. The pattern corresponds nearly but not exactly to that which would be given by a cubic crystal, from which it was concluded by

Bragg and Darbyshire that the material was a "pseudo-cubic form of zinc oxide" instead of the normal hexagonal close-packed form. In the absence of proof to the contrary, the Bragg explanation was accepted and the skin on molten zinc and the film on solid zinc were regarded as zinc oxide and referred to as "Bragg oxide."

G. I. Finch and A. G. Quarrell[2] made a further investigation of the Bragg oxide, mostly on the skin from molten zinc and to a limited extent on solid zinc. They concluded that the film was really that of hexagonal zinc oxide but that the zinc oxide had formed contiguously with the zinc crystals in such a manner as to distort the normal structure, yielding thereby a special diffraction pattern of zinc oxide "basally pseudo-morphic with zinc." A corollary of the Finch and Quarrell explanation is that the Bragg oxide crystals are necessarily oriented in the same position as the substrate zinc crystals.

In direct opposition to their theory, randomly oriented Bragg oxide has been observed in this laboratory on such highly oriented zinc surfaces as rolled zinc, zinc die castings, and single crystal faces of zinc. This evidence and the fact that no one had established by chemical analysis that the Bragg oxide was indeed of the composition ZnO left the question of the composition of Bragg oxide unanswered.

The turning point in the present investigation of the nature of this corrosion product, Bragg oxide, resulted from the detection of Bragg oxide in several samples of pigment, ZnO. The most striking cases were those of pigment, ZnO, that had acquired a carbon dioxide content (as high as 9.9 per cent CO_2 in one case) during accidental storage in an atmosphere of unusually high CO_2 content. The natural deduction from these observations was that the Bragg oxide was some form of zinc carbonate.

Accordingly, a sample of precipitated basic zinc carbonate was prepared and photographed in the electron camera. The close similarity between the diffraction photograms of the precipitated carbonate and the Bragg oxide indicated that the Bragg oxide formed by corrosion was really a basic zinc carbonate and not zinc oxide, a conclusion that was later confirmed by chemical analysis.

The writers advance the suggestion that the samples of skin removed from the surface of molten zinc by Bragg and Darbyshire and by Finch and Quarrell were really ordinary hexagonal zinc oxide when in contact with the molten zinc and that after removal they became converted to basic zinc carbonate by the action of atmospheric carbon dioxide and moisture. This theory will be investigated experimentally.

Electron Diffraction Photograms

Fig. 1 is a reproduction of several electron diffraction photograms typical of the specimens examined in this investigation. A and B are photograms of zinc surfaces corroded by immersion of clean rolled zinc in distilled water saturated with laboratory air at room temperature. (Rolled zinc, 1/8 in. in thickness, was used throughout this investigation. Composition: 0.020-0.046 Pb; 0.005 maximum Cd; 0.009 maximum Fe; 0.001% maximum Cu. The specimens were cleaned by abrading with a fine file and tested for cleanliness in the electron camera prior to the corrosion exposures.) The immersion times were 2 and 3 days, respectively. Specimen A was dried in a current of air for a few minutes; specimen B was dried by placing in a desiccator (Ascarite desiccating agent) for 3 days. The two photograms are essentially the same. The spotted character of B is due to the more bulky nature of the film on this particular specimen, whereby individual reflections from single crystals of the corrosion product were obtained.

Photogram C is of a sample of the water corrosion product removed from the zinc backing. The zinc was immersed in distilled water saturated with air for 7 days, removed from the water and air dried. The resulting bulky white corrosion film was scraped from the underlying zinc and a diffraction photogram of the white powder itself was obtained. (A sample prepared in this manner was also analyzed chemically and was examined by X-ray diffraction. These results will be discussed later.)

Exposure of clean zinc surfaces to moist air produces a corrosion film similar to that produced by water immersion although the rate of attack is quite different. (The data obtained on rate of attack will be presented later in the paper.) Photogram D is from a specimen of zinc that had been exposed to air at room temperature and 33 per cent relative humidity. The diffraction pattern is similar to those yielded by specimens corroded in water immersion.

The electron pattern of precipitated basic zinc carbonate is shown in Photogram E. The pattern is very similar to those obtained from the corroded zinc specimens. This similarity, while not an exact match, led to the conclusion that the corrosion product is basic zinc carbonate, a conclusion well supported by the analytical data to be presented in the following section.

Interplanar spacings, measured by electron diffraction, of the three types of basic zinc carbonate illustrated in Fig. 1 are presented in the table. The three types of basic zinc carbonate represented are (1) the product of the water corrosion of zinc, (2) the product of the corrosion of zinc in air of 33 per cent relative humidity, and (3) the product formed by precipitation from zinc sulphate and sodium carbonate. The striking features of these patterns are the two lines designated "strong." The weaker lines are similar among the three types but not consistently present with the same intensity in all specimens. Reasons for these dissimilarities are suggested in the section following.

The essential role of carbon dioxide in the ordinary corrosion of zinc is further demonstrated by experiments conducted in the absence of carbon dioxide, under which conditions the corrosion film was entirely different, being zinc oxide and not basic zinc carbonate. These experiments will be described more fully later but Photogram F is included at this point to illustrate the result obtained. The specimen of Photogram F was obtained by immersing zinc in distilled water saturated with carbon dioxide free air and then drying in carbon dioxide free air. The corrosion film is hexagonal zinc oxide, showing a high degree of preferred orientation of the crystals with their basal planes parallel to the zinc surface. This specimen was immersed 2 hrs., longer immersions tending to give a randomly oriented zinc oxide film.

Composition of the Corrosion Product

A large sheet of zinc was placed in a beaker of distilled water. The beaker was covered with a cover glass and allowed to stand in the laboratory for three weeks. The zinc was then removed, air dried for several hours and the white corrosion products were gently removed wth a spatula. The chemical analysis of this material was as follows:

	Percent
Total Zn as ZnO	71.8
Total CO_2	9.4
H_2O	14.0
	95.2

(The H_2O was determined by subtracting the CO_2 content from the loss on ignition, 23.4 per cent.)

The ratio of ZnO to CO_2 calculates quite closely to $4ZnO.CO_2$. (In a later section of this paper, in discussing the mechanism of formation of the corrosion product, evidence is cited to show that the initial product of corrosion is zinc oxide. The zinc oxide then becomes carbonated by action of carbon dioxide and water, the action proceeding from the surface of the zinc oxide particles inward. It is possible that the corrosion product of which the analysis is given above may be only partially carbonated and that the CO_2 content of the outside of the particles may be higher than the inside. In this case the ratio $4ZnO.CO_2$ must be regarded as an average composition.) On this basis the water content is nearly 4 molecules, so that the empirical formula of this product can be written $4ZnO.CO_2.4H_2O$. An alternative manner of writing the formula would be $ZnCO_3.3Zn(OH)_2.H_2O$. Evidently this corrosion product is to be regarded as a basic zinc carbonate with the manner of combination of the H_2O uncertain. The observed differences in the electron patterns among several specimens in number and intensities of the diffraction rings may be due to differences in the state and degree of hydration or carbonation. The existence of such differences is to be expected since the drying and degree of carbonation of the specimens can hardly be duplicated in every case. The corrosion product could not be dried by heating, owing to the danger of driving off some carbon dioxide. The corrosion product may be completely decomposed by heat to zinc oxide according to experiments that will be described later.

During the course of this work, a recent publication was noted in which are reported the results of a similar chemical analysis. Martial-Felix Taboury and Elie Gray[3] corroded zinc in water in the presence of and also in the absence of air. In the absence of air the product was reported as zinc hydroxide. In the presence of air a short-time immersion produced a product having the empirical formula $3ZnO.CO_2.2H_2O$ and after an immersion of more than 3 months the product had the composition $4ZnO.CO_2.3H_2O$.

The composition of precipitated basic zinc carbonate was investigated on three independent samples. The original samples were thoroughly washed free of soluble carbonates and dried in a desiccator before analysis. Two of these samples were made by precipitation from zinc sulphate with sodium carbonate and the third by dilution of an amino-zinc carbonate solution with water. Each of the three samples yielded, by chemical analysis, the empirical formula $5ZnO.2CO_2.4H_2O$. The precipitated product appears to be carbonated to a higher degree than the zinc corrosion product, a factor which probably accounts for the differences between the electron diffraction patterns of the two forms as illustrated in Fig. 1.

Mechanism of Formation of the Water Corrosion Product

Some of the corrosion product obtained by immersing zinc in distilled water saturated with air for several days was removed from the zinc backing and examined by electron and X-ray diffraction and ana-

Fig. 1—Electron Diffraction Photograms of Zinc Corrosion Product

A. Zinc immersed 2 days in distilled water, air dried. B. Zinc immersed 3 days in distilled water, dried 3 days in desiccator. C. Corrosion product scraped from zinc after 7 days' immersion in distilled water. D. Zinc exposed 79 days to air at room temperature and 33 per cent relative humidity. E. Precipitated basic zinc carbonate ($ZnSO_4 + Na_2CO_3$, washed free of water soluble carbonates). F. Zinc immersed 2 hrs. in distilled water saturated with CO_2 free air, dried 2 hrs. in CO_2 free air. (This photogram corresponds to hexagonal zinc oxide oriented with the basal plane parallel to the zinc surface.)

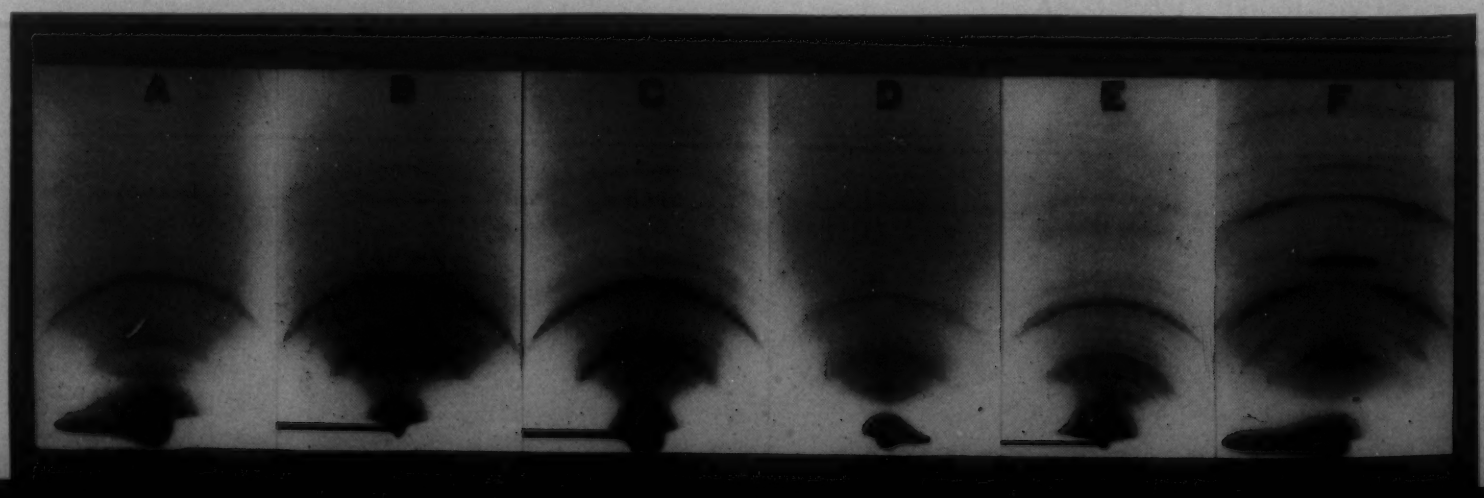


Table of Interplanar Spacings and Relative Intensities of Basic Zinc Carbonate

Formed by Water Corrosion of Zinc		Formed by Air Corrosion of Zinc		Formed by Precipitation	
Spacing	Intensity	Spacing	Intensity	Spacing	Intensity
3.4	Weak	3.2	Weak	3.2 A	Moderate
3.1	Weak	2.9	Weak	2.9	Weak
				2.8	Moderate
2.9	Strong	2.7	Strong	2.5	Strong
2.7	Moderate	2.5	Moderate		
2.4	Weak	2.1	Weak	2.2	Weak
2.2	Weak	1.82	Weak	1.92	Moderate
2.0	Moderate	1.70	Weak	1.67	Weak
1.61	Strong	1.56	Strong	1.55	Strong
1.39	Moderate			1.34	Moderate
1.19	Moderate			1.28	Weak
1.03	Moderate			1.01	Moderate
0.92	Moderate			0.89	Moderate

Note: These measurements were referred to ZnO as a calibration standard, whose spacings are accurately known. The principal source of error, however, is in maintaining constant voltage. Errors from this source may have amounted to as much as 1-2 per cent in the above measurements. Since carrying out the experimental work of this paper the voltage stability has been improved so that errors from this source have been reduced to 0.5 per cent or less. The latter precision is necessary in the extension of corrosion studies to outdoor weathering where the corrosion product may be basic zinc sulfate, as in industrial exposures. The basic zinc sulfate gives a diffraction pattern similar to the basic zinc carbonate, the most readily distinguishable feature being the outer strong ring which has a spacing of 1.56 to 1.60 A in the carbonate formed by outdoor corrosion and a spacing of 1.50 to 1.55 A (usually resolved as two rings) in the sulfate formed by outdoor corrosion.

lyzed for CO_2. By electron examination, the basic zinc carbonate structure was indicated, by X-ray diffraction the material appeared to be mostly hexagonal ZnO with some basic zinc carbonate, by chemical analysis the CO_2 content was 5.6 per cent.

This experiment indicates that the initial corrosion product is zinc oxide (or perhaps zinc hydroxide decomposing to zinc oxide before X-ray examination) which subsequently becomes carbonated to basic zinc carbonate. This particular product was evidently in the form of zinc oxide coated with basic zinc carbonate since the electron examination showed only the coating of the particles, basic zinc carbonate, and the X-ray examination revealed the total structure, zinc oxide plus basic zinc carbonate. A repetition of this experiment revealed basic zinc carbonate only by both electron and X-ray examination. Evidently, in the latter case complete carbonation had been effected.

The fact that water and air in the absence of carbon dioxide produce a zinc oxide corrosion product is in agreement with the theory expressed above that zinc oxide is the initial corrosion product which in the presence of CO_2 and H_2O becomes converted to basic zinc carbonate.

Behavior of the Corrosion Product on Heating

A sample of the water corrosion product was heated one hour at 100, 200, and 300 deg. C. By electron diffraction the sample was found unchanged at 100 deg. V., became partially converted to ZnO at 200 deg. C., and became completely converted to ZnO at 300 deg. C. Corresponding X-ray examination indicated the complete conversion to take place as low as 200 deg. C. Similarly, precipitated basic zinc carbonate loses most of its CO_2 by heating at 300 deg. C. One of the samples of pigment zinc oxide that had acquired CO_2 during storage dropped from 9.9 to 0.32 per cent CO_2 on heating 1 hr. at 300 deg. C. These facts are consistent with the identification of the corrosion product as basic zinc carbonate.

Rate of Formation of Basic Zinc Carbonate Film

The changes undergone by a clean zinc surface under various exposure conditions and for various lengths of exposure were studied. Exposures were made in air at 33 and 75 per cent relative humidity, room temperature, and in water at room temperature. The air exposures were made in closed desiccator jars, the air in which was controlled at a definite relative humidity by means of a saturated solution of a salt in contact with excess salt contained in the well of the desiccator jar. No provision was made for air circulation, the only opportunity for a change of air in the jars being when the zinc specimens were removed for examination at intervals. The salt used in the 33 per cent R.H. container was $MgCl_2.6H_2O$ and in the 75 per cent R.H. container was NaCl. The water corrosion specimens were immersed in a beaker of distilled water, the specimens being dried in a stream of air before each inspection. In each series of exposures the specimens were exposed cumulatively, being removed from the exposure at selected intervals for inspection and then replaced.

Immersion in water for 5 sec. produced no apparent change but after 30 seconds' exposure the zinc was coated with a film of basic zinc carbonate sufficiently complete to prevent the electron detection of metallic zinc. Immersion and inspection were continued at various intervals up to 40 days with apparently no further change except in the quantity of corrosion product.

Another pair of specimens was immersed in water 3 days and then placed in a desiccator with Ascarite (a proprietary desiccating agent with sodium hydroxide as the essential ingredient) as the desiccating agent. (Ascarite should remove both CO_2 and H_2O from the jar.) Examined at various intervals up to 28 days the corrosion product remained unchanged, as basic zinc carbonate. Examined once more, after 84 days in the desiccator, the basic zinc carbonate appeared to be partially decomposed since hexagonal zinc oxide as well as basic zinc carbonate was detected.

Specimens exposed to air at 33 per cent relative humidity appeared unchanged after one day but after 2, 3, 4, and 9 days' exposure the electron examination indicated basic zinc carbonate as well as zinc at the surface of the specimens. After 14, 21, 28, 36, 49, 79, and 106 days the specimens were sufficiently coated with basic zinc carbonate to prevent the detection of the zinc substrate.

The behavior of specimens exposed to air at 75 per cent relative humidity differed in two respects from those exposed at 33 per cent. The basic zinc carbonate film formed and apparently completely covered the zinc exposed at 75 per cent relative humidity in from 1 to 6 days (differing in rate among 4 specimens) and the basic zinc carbonate showed a preferred orientation. In one pair of specimens the preferred orientation persisted, the last inspection being after 97 days' exposure and in another pair of specimens the orientation disappeared after 21 days, being randomly oriented at 21, 35, and 91 days' exposure. These experiments indicate that the physical structure of the carbonate film varies with the humidity.

Two clean zinc specimens were placed in the Ascarite desiccator and removed occasionally for electron examination. The corrosion of the zinc was greatly retarded under these conditions. Some basic zinc carbonate was detected after 14, 28, 42, and 55 days but the film was not sufficiently complete to mask the underlying zinc until 98 days of exposure. In spite of the fact that the Ascarite removes both CO_2 and H_2O from the desiccator jar, the specimens became corroded. The admission of corroding gases took place each time the desiccator was opened for the removal of these or other specimens and at the time of each electron examination the specimens were exposed to the laboratory air for a few minutes, circumstances which probably explain why the specimens corroded.

The exposures at approximate relative humidities of 0, 33, and 75 per cent demonstrate the marked influence of water vapor on the rate of formation of the basic zinc carbonate coating. The degree of humidity may exert its influence in accelerating the rate of formation of the initial product, zinc oxide, and may also affect the rate of subsequent carbonation of the zinc oxide.

Water Immersion in Absence of Carbon Dioxide

The marked difference in the nature of the water corrosion film depending on whether or not CO_2 is present has been discussed earlier in this paper. A number of experiments were tried under CO_2-free conditions. The experimental procedure was as follows:

Distilled water was placed in a 500-cc. Erlenmeyer flask and boiled for 2 hrs., the final volume being about 150 cc. Freshly cleaned zinc specimens were lowered into the water immediately after removal of the flask from the hot plate. The mouth of the flask was then closed with a rubber stopper fitted so that CO_2-free air could be continually bubbled through the water. During the passage of the air through the water the latter cooled to room temperature and remained at that temperature for the duration of the exposure. At the end of the exposure the water was ejected from the flask through a glass tube by applying pressure to the CO_2-free air. The water adhering to the specimens and to the walls of the flask after this ejection was evaporated by passing dry CO_2-free air through the apparatus. At the completion of the drying the specimens were removed and immediately transferred to the electron camera.

It should be noted that while the intent of this experiment was to duplicate the other water immersion tests except that CO_2 was omitted, one other difference existed, since the water was hot at the time of immersion of the zinc. The water cooled to room temperature during the immersion but it is possible that the initial immersion in hot water may have altered the type of corrosion from that which would otherwise have been obtained.

Four runs, two specimens of zinc in each, were successfully made in this apparatus, the success being judged by the fact that the corrosion films indicated no evidence of carbonation. In two runs, the immersion time was 2 hrs., the drying time 2 hrs.; in one run the immersion time was 3 hrs., the drying time 2 hrs.; and in one run the immersion time was 16 hrs., the drying time 24 hrs. The three short-time immersions produced the highly oriented zinc oxide film and the long-time immersion produced a randomly oriented zinc oxide film.

Discussion

The corrosion experiments reported in this paper are based entirely on laboratory tests. It seems likely that similar phenomena take place during outdoor exposure, complicated, of course, by ever changing weather conditions and the presence of corrosive gases other than those experienced in these laboratory experiments. Extension of these studies to zinc specimens corroded out-of-doors is now being made and preliminary results indicate that the product of outdoor weathering may be basic zinc carbonate, basic zinc sulphate or both. Under certain conditions, chlorides may be detected in the outdoor corrosion products.

Summary

1. The product of the water corrosion and that of the indoor atmospheric corrosion of zinc has been identified as basic zinc carbonate by means of electron and X-ray diffraction supported by chemical analysis of the water corrosion product.

2. The composition of the water corrosion product was found to be $4ZnO.CO_2.4H_2O$. Evidence was obtained to indicate that the composition may vary somewhat depending upon circumstances.

3. Evidence was obtained to indicate that zinc oxide (or hydroxide) is the initial product of water corrosion, the oxide being subsequently converted by the action of carbon dioxide and water to basic zinc carbonate.

4. A coating of basic zinc carbonate is formed by

only 30 seconds' immersion of zinc in water, sufficiently complete to prevent the detection of the electron diffraction pattern of the underlying metallic zinc.

5. The time required for the formation of a film by atmospheric corrosion complete enough to obscure the zinc substrate becomes less as the relative humidity is increased, ranging from 98 days in a nominally dry atmosphere to 14 days in air at 33 per cent relative humidity and to 1 to 6 days in air at 75 per cent relative humidity.

6. Water immersion in water saturated with carbon dioxide free air produced a zinc oxide coating.

Acknowledgement

The writers express appreciation to C. E. Reinhard for helpful discussions in planning this investigation and in interpreting the results, and to B. A. Shippy and O. A. Short for their assistance in the preparation of precipitated basic zinc carbonates.

References

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[2] G. I. Finch and A. G. Quarrell, *Proc. Phys. Soc.* (London) Vol. 46, p. 148 (1934).
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Stainless Clad Steel by a Unique Process

A METALLURGICAL ENGINEERING PROBLEM in bonded bi-metallic plate is announced as having been solved by the Babcock & Wilcox Co. New York. Usually regarded as a difficult one, it is claimed solved in a simple and unique manner.

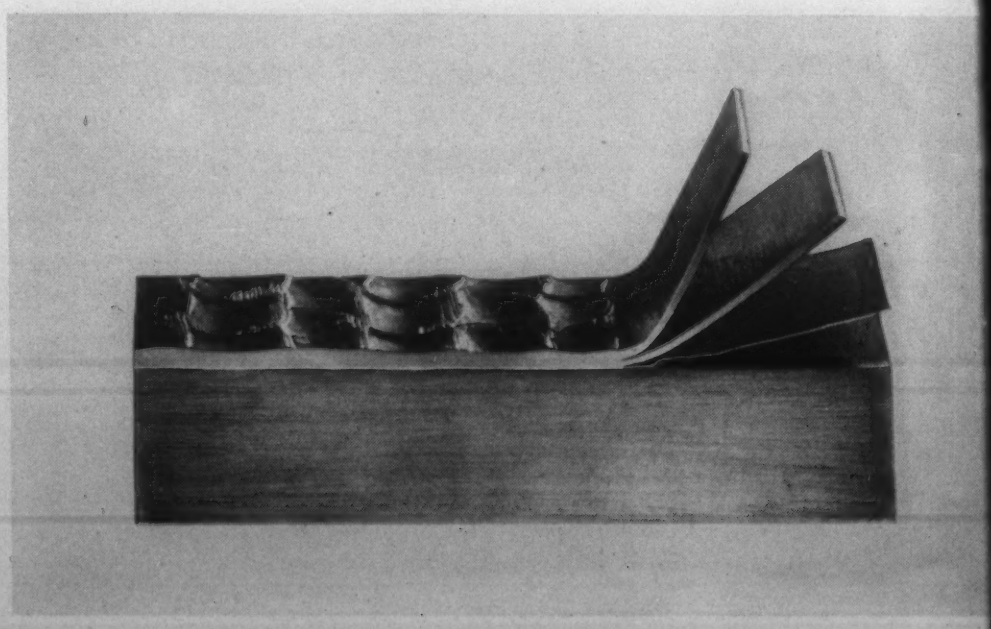
The problem which technicians of the company tackled was: If a veneer of corrosion-resistant alloy can be bonded over the entire surface of a carbon steel plate with the prevention of carbon migration from the base metal to the alloy, both in the bonding operation and in subsequent service, a product will result having the greatest potentiality for service inherent in a bi-metallic plate.

A manufacturing process by which these results can be accomplished economically and consistently is announced as a result of research to solve the problem. A plate is being manufactured which is claimed to "meet the economic expectations of those who use composite plate to get structural strength with the relatively inexpensive carbon" or low-alloy steels, "and resistance to corrosion with far less alloy steel than would be the case if the alloy had to provide both strength and corrosion resistance." Such alloy-bonded plate is suitable for use in pressure vessels or other process equipment for oil refinery and chemical plant services.

An Important Factor is Welding

Welding is an essential factor in the process of making "B & W Croloy Plate," the composite plate that resulted from this investigation. It is composed of thin layers of chromium alloy steel (12 to 14 or 16 to 18% Cr) electric resistance-welded to a base plate of carbon or carbon-molybdenum steel by individual spot-welds that overlap lengthwise and crosswise of the plate, bonding the alloy to the plate over the entire surface—stated to be "the only

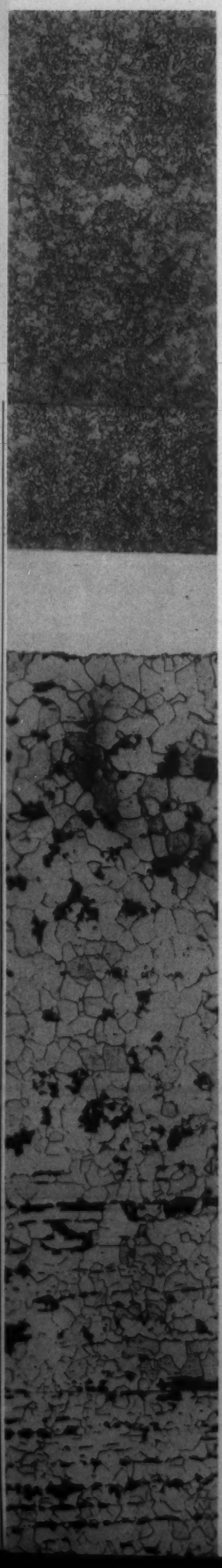
The bonded plate with the alloy veneer of known and uniform thickness obtained by electric resistance welding two or more thin rolled sheets of chromium alloy to a relatively inexpensive base plate of carbon or carbon-molybdenum steel with a sheet of nickel between.



process by which the alloy layer is electric resistance-welded to the base metal without leaving unbonded areas."

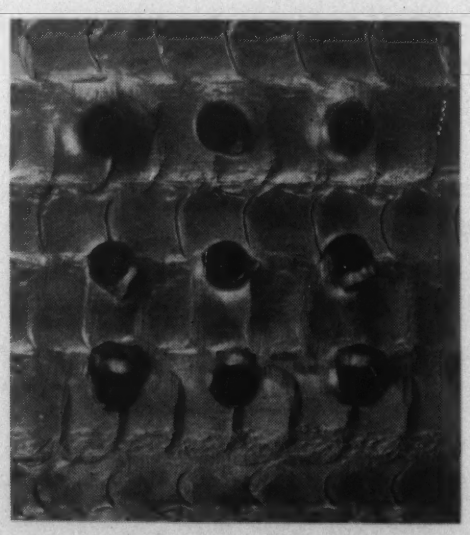
The process is made possible by the use of two or more sheets of alloy (stainless) steel with a sheet of nickel between the alloy and the base metal. The company states that this construction provides the resistance to flow of the welding current necessary for the generation of welding heat because of the several areas of contact between the electrodes and the base metal, each contact area increasing the resistance and, hence, the temperature. The pressure necessary on the alloy sheets to complete the bond is also reduced because the alloy sheets are thin and can, therefore, be pressed into place during the welding operation with lower pressure than would be neces-

Curled chip machined from the bonded plate shows that even this severe deformation does not cause failure of the bond.

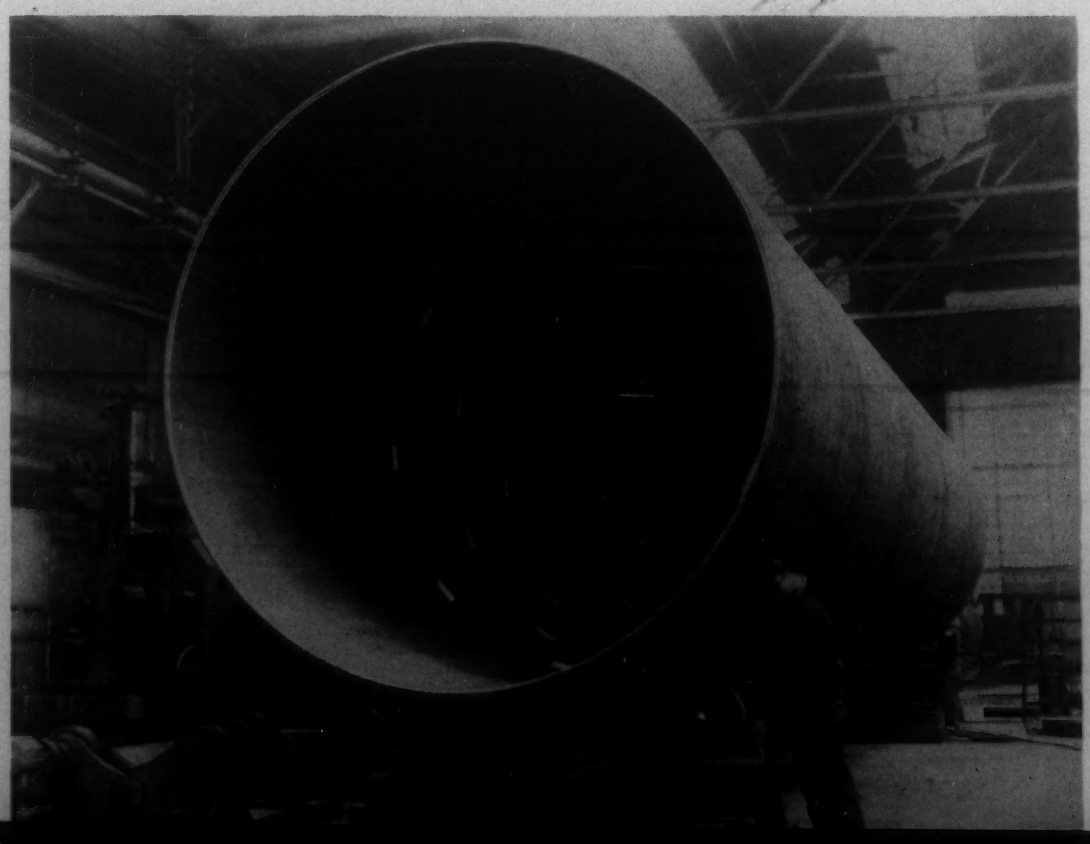


(Left) Micrographs of the bonded plate show that the nickel layer prevents formation of a band of chromium carbide usually resulting from the welding of chrome steels to carbon steels due to carbon migration from the base steel to the alloy. Evenness of the nickel layer and absence of grain growth are evident.

(Below) Severe deformation of the alloy layer of the bonded plate caused by twisting and inside bending failed to cause cracking or separation of the alloy layer from the base metal.



(Left) Permanence of the bond demonstrated by the punch test. In this test a square-nosed punch, inserted in holes drilled through the base plate and flat-bottomed at the alloy layer and then punched, failed to tear the alloy from the base plate, even with ligaments of only 1/2 in. between the holes but made clean punctures in the alloy.



Shell of refinery coke chamber formed of the new type stainless clad steel. The shell diameter is 12 ft. and length 50 ft. with the plate thickness 1 1/16 in. Strength and permanence of bond permits welding of alloy clips for internal fittings directly to the bonded lining of the vessel.

sary with a single alloy layer of equal thickness. This results in less distortion than would be the case with the single alloy steel layer applied with the correspondingly greater pressure while the metal is hot and therefore more readily deformed. Bonded plates of this character can be produced in the largest width and length of base metal obtainable and fabricated into large vessels, etc.

Permanence of the Bond

Permanence of this special method of bonding has been demonstrated by a series of physical tests. But soundness of the bond is claimed attained in another and more important way—the use of nickel between the base metal and the corrosion-resistant alloy steel. "Since nickel does not have an affinity for carbon as has chromium, the nickel prevents migration of carbon from the base metal to the alloy steel," preventing the formation of a bond of chromium carbide which otherwise usually forms. "Thus interface precipitation of carbides, with resultant susceptibility of the lining to corrosion embrittlement when the material is subjected to high temperature, is prevented."

Each plate, thus bonded, receives a normalizing treatment at 1650 deg. F. to improve the quality of the parent carbon or carbon-molybdenum steel and induce toughness in the alloy steel—another test of the bond in that buckling does not result.

Illustrations accompanying this brief article explain some of the properties of this stainless clad steel. —E. F. C.

EDITORIALS

(Continued from page 259)

or what not; might be considered as possible ways of demonstrating the presence of "protective plasticity" of the proper type and amount. Unfortunately, most such determinations involve considerable work and hence are handicapped in competition with the lazy man's way—evaluating the material on the basis of percentage elongation and trusting to God that the figure means something in the particular service to be encountered.—H.W.G.

Spectrographic Analysis

The use of spectrography by American industry has been accelerated markedly in recent years, and particularly in the last few months. Two large plants are now controlling their metal production by spectrographic analysis. One of them is working two shifts. A well-known, long-established consulting laboratory in New York City is doing commercial and research work in this field. A Russian scientist, long in this country and widely traveled and educated, told us in a recent conversation, that spectrography in America should have come long ago. Add to this the fact that Dr. H. Kaiser, of Carl Zeiss, Jena, Germany, has been making an investigation of the future of the spectrograph in this country.

Interest in this subject is so keen that the American Society for Testing Materials, at its last annual meeting, scheduled a round-table discussion on spectrographic analysis lasting a day. It was well attended and was addressed generously by Dr. Kaiser of Germany. This meeting was planned as the forerunner of a symposium in June, 1940.

This should have the support of all interested. It is a complex subject involving physics, mathematics, electricity, metallurgy, chemistry and so on. But the A. S. T. M. is equal to the occasion, and the final result will be a thorough thrashing out of all the angles and probably suitable specifications to guide industry.—E. F. C.

Tin

The metal tin is one of the raw materials essential to American industry. It is a strategic metal—without which, in war or not—we would be in serious straits. Readers of this magazine do not need to have this demonstrated.

Because of the operations of Japan's war machine in the Far East and because of the extent to which these have gone, we hear predictions that China is not the only territory on which Japan has set its heart. There is the possibility that the East Indies—or at least their domination and control—are a goal. From that part of the world comes most of our tin and rubber.

We in the metal industry are most concerned about tin. As an illustration of the quantity which is imported into the United States, mostly for consumption in the canning, bearing, bronze and other industries, our official statistics show that, for 1937, 1938 and the first quarter of 1939 (27 months), over 340,683,000 lbs. or more than 175,340 net tons were imported, at a valuation of over $163,385,700—an impressive total! This tin came in as "bars, blocks, pigs, etc."

It may be a case of "borrowing trouble" to speculate on conditions which would result from Japan's domination of the main source of our supplies of tin. But it is an eventuality and should be watched. In that case, substitutes for tin would be of inestimable value.

Is not the development of such substitutes a problem for metallurgists to seriously consider—and not too late?—E.F.C.

Progress in Malleable Iron

We were rather astonished to learn recently that the number of malleable iron foundries, which totaled about 175 a few years back, is now approximately only 75. In reply to the question "why?" it was stated that the industry has been asleep—not sufficiently research and technically minded. Yet this industry has consistently raised the quality of its product, specifications of 1915 requiring only 5 per cent elongation and present-day manufacture is able to produce material of over 20 per cent as Touceda stated in an article—"What is Made of Malleable Iron?" METALS AND ALLOYS, Vol. 9, June 1938, pages 151-156.

Whether or not the allegation is true, it is quite interesting to learn that technical progress in the industry is broadening. Arrangements have been made for an eight weeks' course in malleable foundry practice and metallurgy, open to employees of all members of the Malleable Founders' Society. All expenses for the course, except living costs, are to be paid by the companies. Also the organization is now decidedly active in promotion of technical developments.

There is no reason why this branch of the foundry industry should not parallel, in a measure at least, the modern history of technical progress in the gray iron industry.—E. F. C.

Metals at Low Temperatures

The interest in the properties of metals at low temperatures (considerably under zero Fahrenheit) is increasing. This was in evidence during a round-table discussion on this subject at the annual meeting of the American Society for Testing Materials in June. A whole evening's session was devoted to this.

Increasing use of equipment involving metals and alloys at temperatures around minus 50 deg. F. and lower has developed. This is true in such industries as the oil (de-waxing), the helium, the airplane (for high altitudes), the railroad (in cold climates), the refrigeration and so on. Such temperatures affect the properties of metals and alloys, adversely in some cases. Certain compositions have unusually satisfactory properties to meet such conditions. Alloy steels are already to the fore in this, nickel being prominent. But the knowledge on this subject is not voluminous, and it was evident from the discussions that much work needs to be done.

The Society has every facility for pursuing investigations in this comparatively new field. This round-table is intended to be the forerunner of a symposium at the annual meeting in 1940. The highly valuable work which the Society's joint committee has done in recent years, in the opposite field of high temperatures, assures a thorough job in this new work.—E. F. C.

Scotland Yard to the Rescue

In a letter to the editor in the May *Bulletin* of the American Ceramic Society, Dr. Sosman comments on the lack of knowledge of the source of those inclusions in steel which appear to be due to the nozzle, stopper, ladle lining or what not, rather than to the deoxidation reactions of the steel itself.

He suggests that positive proof as to which is the culprit could be obtained by making up experimental nozzles, linings, etc. from refractories in which radioactive materials, such as compounds of thorium or uranium are incorporated. Radioactivity is not affected by temperature, so an inclusion coming from that single source which has been provided with the radio active indicator, could be identified as such by its action on a photographic film.

While this suggestion has naturally been addressed to the ceramists who would make up the refractories, it is worth calling to the attention of metallurgists who would carry on once the refractories were provided.—H. W. G.

Attendance at Conventions

Convention attendance has made a rather unusual record this year. Three technical gatherings—in April, May and June, respectively—reported record registrations.

The last one was the annual meeting of the American Society of Testing Materials at Atlantic City in June—the registration of over 1350 topped all records for the Atlantic City gatherings. The others were the Open-hearth meeting in Cleveland in April, and the large convention (non-show) of the American Foundrymen's Association in Cincinnati in May. Both of these made new attendance records. In all these three meetings, interest in the technical programs was highly noticeable.

We have heard several suggested explanations of this phenomenon. One is that, because of only partial plant operations, more time is available for such meetings. Another is that executives feel that, if the money is not spent in this manner, the Government will get it anyhow. Still another is that interest in technical matters is expanding, assuring large attendance under any economic or political conditions.

We leave the reader to make his own decision, though we feel sure that the high grade programs are a major factor.—E. F. C.

Herbert M. Boylston

With deep regret we learn of the death of H. M. Boylston. His name and his work are well known to all American metallurgists. His association with Dr. Albert Sauveur in the early days of the development of metallography will long be remembered and appreciated. "Sauveur and Boylston" is a phrase which means much to American metallographists as a landmark in metallurgical progress.—E. F. C.